CONSTITUTIONAL DIAGRAMS
OF
URANIUM AND THORIUM
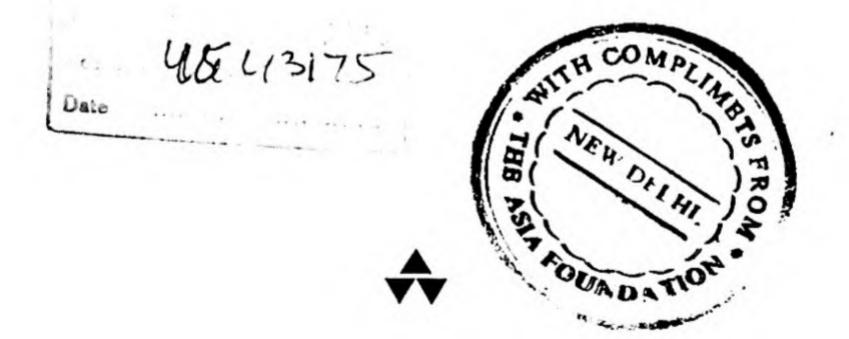## ALLOYS

by

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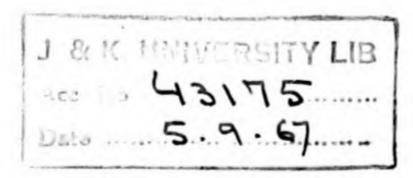THE SHIPPINGPORT PRESSURIZED WATER REACTOR

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THORIUM BINARY SYSTEMS

THORIUM TERNARY SYSTEMS

PREFACE

This book supersedes the Battelle Memorial Institute publication "Compilation of US and UK Uranium and Thorium Constitution Diagrams" (BMI-1000). It is a new reference piece in a modified format. The original Compilation has been used extensively and has been reprinted. The present authors believe that this degree of acceptance of the original work implies acceptance of the concept and approach. As a result, they have undertaken this new work in an attempt to provide an even more useful reference piece. Like its predecessor, this work was written with the cooperation of representatives of the United Kingdom.

The modified *Metals Handbook* system of notation for the diagrams employed in BMI-1000 was again used in preparing these constitutional diagrams. The symbols a/o for atomic per cent and w/o for weight per cent have been used. In keeping with the general convention, phases have been designated beginning with the base. The inconvenience of having two alpha phases, alpha A and alpha B, in the system A — B is thereby obviated. Some slight but easily reconciled confusion may exist with previous data where the diagram may have been developed for the system B — A.

This book is divided into two major sections, uranium alloys and thorium alloys. The major sections are preceded by a discussion of the transformation and melting temperatures of the base metal. Following the discussion are the various systems in alphabetical order. The major sections include both binary and ternary systems. In the previous edition the systems were separated on the basis of whether or not constitutional diagrams were available. For this book it was determined that less weight should be given to the presence or absence of a diagram and that utilization of the information was most readily accomplished by a completely alphabetical listing.

Generally, only unclassified references have been used. However, because the unclassified literature is incomplete for several systems, some classified references are given. It is believed that future declassifications may make many now-classified references readily available.

The authors dedicate this volume to the late Henry A. Saller, one of the original editors. His interests and efforts in bringing the original Compilation into being have made the writing of this book a much more straightforward task.

ACKNOWLEDGMENTS

MELTING POINTS AND ALLOTROPIC MODIFICATIONS OF URANIUM

Reliable reports of the melting point and transformation temperatures of uranium are available in the literature [1].* Further, uranium of ultra-high purity has been prepared and studied by thermal analysis [2]. The melting point and transformation temperatures which were determined are shown below.

	Temperature, C		
	Heating	Cooling	Average
Melting point	1128.7	1129.0	1128.9
Beta-gamma transformation	772.1	766.7	769.4
Alpha-beta transformation	667.1	657.7	662.4

In order to standardize the construction of diagrams, the average values shown above have been used throughout this volume as the transformation temperatures and melting point of uranium.

The crystal structure of alpha uranium has been determined to be orthorhombic by Jacob and Warren [3], using x-ray powder methods. The data on alpha in the tabulation on page 2 are from their work. Study by Lukesh [4] has confirmed these data on single crystals or uranium.

The structure of alpha uranium may be regarded as being formed by the stacking of corrugated sheets. The binding within the corrugated sheets is largely covalent in nature [5].

The crystal structure of beta uranium is complex and of tetragonal symmetry. Although it was not until recent years that the structure was known to be tetragonal, the major contributors are now in reasonably close agreement about it. The analysis of the structure of beta uranium has been accomplished by two different techniques. Tucker [6] has studied it at room temperature, using single crystals of retained beta in a 1.4 a/o chromium alloy. Thewlis [7] has studied beta both in pure uranium and in the 1.4 a/o chromium alloy at 720 C by high-temperature powder techniques.

Thewlis [7] reports that there are differences in intensity between beta powder patterns of the pure metal and those of the low-chromium alloy at 720 C. Tucker and Senio [8] report that the major discrepancy reported by Thewlis for the powder pattern of the low-chromium alloy is not found

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* See references at the end of each section.

in single-crystal data from a sample of identical composition. On this basis, Tucker and Senio [8] conclude that the patterns of the beta structure for the low-chromium alloy and for the pure metal are identical.

The lattice dimensions for beta tabulated below are from Thewlis [7], while the other data for beta are from Tucker and Senio [8]. Tucker [6] reports unit-cell dimensions for single crystals of the 1.4 a/o chromium beta at room temperature to be $a = 10.52$ and $c = 5.57$ A, with a measured density of 18.697 g/cm^3. Similar data are reported by Thewlis [7], who gives lattice constants of $a = 10.590 \pm 0.001$ and $c = 5.634 \pm 0.001$ A and a density of 18.56 g/cm^3. These latter data are probably the more precise, since they were obtained by means of powder techniques. At 720 C, the unit-cell dimensions of the 1.4 a/o chromium beta, according to Thewlis [7], are $a = 10.763 \pm 0.005$ and $c = 5.652 \pm 0.005$ A, corresponding to a density of 17.93 g/cm^3.

The structure of gamma uranium has been shown to be body-centered cubic. The data tabulated below are from Thewlis [10]. X-ray data were obtained at 800 C, giving a lattice constant of $a = 3.487$ A [9].

Lattice constants were also determined for a series of alloys containing 17.3 to 31.2 a/o molybdenum which possessed a retained-gamma structure [9]. A lattice constant of $a = 3.474$ A at room temperature was determined by extrapolation of these data. Vegard's law was assumed to apply to this system.

| Phase | Unit cell | | | Density, g/cm^3 | | Space group | Remarks |
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Alpha	Ortho-rhom-bic	$a = 2.852$ $b = 5.865$ $c = 4.945$	4	19.12		Cmcm	
Beta	Tetrag-onal	$a = 10.759$ ± 0.001 $c = 5.656$ ± 0.001	30	18.11		P4/mnm	Data for 720 C
Gamma	Bcc	$a = 3.524$	2	18.06		Im3m	Data for 805 C

References
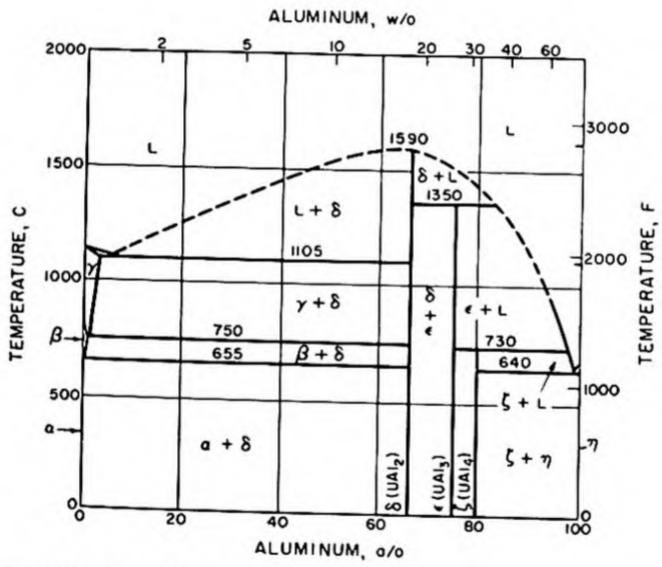
1. A. I. Dahl and H. E. Cleaves, "The Freezing Point of Uranium," *J. Research Natl. Bur. Standards*, **43**, 513–17 (1949).

2. J. E. Baumrucker and H. H. Chiswick, unpublished information (March, 1953).

3. C. W. Jacob and B. E. Warren, "The Crystalline Structure of Uranium," *J. Am. Chem. Soc.*, **59**, 2588 (1937).

4. Joseph S. Lukesh, "Note on the Structure of Uranium," *Acta Cryst.*, **2**, 420 (1949).

5. C. W. Tucker, Jr., "The Crystal Structures of Metallic Uranium," *Trans. Am. Soc. Metals*, **42**, 762–70 (1950).

6. C. W. Tucker, Jr., "The Crystal Structure of the Beta Phase of Uranium," *Acta Cryst.*, **4**, 425–31 (1951).

7. J. Thewlis, "X-ray Powder Study of Beta-Uranium," *Acta Cryst.*, **5**, 790–94 (1952).

8. C. W. Tucker, Jr. and Peter Senio, "An Improved Determination of the Crystal Structure of Beta Uranium," *Acta Cryst.*, **6**, 753–60 (1953).

9. A. S. Wilson and R. E. Rundle, "The Structures of Uranium Metal," *Acta Cryst.*, **2**, 126–27 (1949).

10. J. Thewlis, "Structures of Uranium," *Nature*, **168**, 198–99 (1951).

URANIUM-ALUMINUM

The Constitutional Diagram

There is virtually complete agreement on the uranium-aluminum system. The diagram shown is that of Gordon and Kaufmann [1], modified to include the UAl₄ intermetallic compound reported by Borie [2] and Allen [3].

Minor differences exist between this diagram and that of Allen [3]. These differences consist of small variations in the liquidus and in the various reaction isotherms. For example, at the uranium end of the

system, Allen [3] reports values of 1123, 757, and 672 C for the eutectic and eutectoid isotherms. These values correspond to 1105, 750, and 655 C, respectively, in the diagram shown here. The work of Saller [4] is in agreement with the diagram shown. Thermal-analysis techniques resulted in slightly higher values for the aluminum-rich liquidus with UAl_3, as reported by Storhok and Bauer [5]:

755 C	17 w/o uranium
855 C	20 w/o uranium
954 C	24.5 w/o uranium
1068 C	30.9 w/o uranium
1190 C	41.7 w/o uranium
1265 C	51.2 w/o uranium

Some details of the solubility of aluminum in uranium have been reported by Allen [3]:

980 C	0.5 w/o aluminum
800 C	0.2 w/o aluminum
700 C	0.11 w/o aluminum
650 C	<0.1 w/o aluminum

Similar values, perhaps slightly lower, can be scaled from diagram in the gamma-uranium region.

CRYSTALLOGRAPHY

The crystallography of the intermetallic compounds is summarized in the tabulation below. The data shown for UAl_2 and UAl_3 are from the work of Rundle and Wilson [6]. The structure of UAl_3 is confirmed by Maskrey and Frost [7], although they report a lattice dimension of $a = 4.27$ A. They also report that the atom positions of UAl_3 are surely those of the $AuCu_3$ ordered structure. On the basis of intensity data, it appears that a high degree of order exists in UAl_3.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta (UAl_2)	Fcc	$a = 7.811$	8	8.14	8.2	Fd3m	C15-type Cu_2Mg structure
Epsilon (UAl_3)	Simple cubic	$a = 4.287$	1	6.8		Pm3m	Ordered, $AuCu_3$-type structure
Zeta (UAl_4)	Ortho-rhombic	$a = 4.41$ $b = 6.27$ $c = 13.71$	4		5.7 ± 0.3	Ima or Imma	

Borie studied UAl_4 (once identified as UAl_5 [1]) by both x-ray and neutron diffraction.[2] Chemical analyses and density measurements were somewhat inconsistent with the UAl_4 stoichiometry and structure. However, this inconsistency is explained on the basis of a defect lattice where some of the uranium sites are unoccupied or are occupied by aluminum atoms. Analysis of the structure revealed that it can be described as plates of the cubic UAl_3 structure held together by extra aluminum atoms [2].

References

1. P. GORDON and A. R. KAUFMANN, "The Alloy Systems Uranium-Aluminum and Uranium-Iron," *J. Metals*, **2**, (1) 182 (1950).

2. B. S. BORIE, JR., "Crystal Structure of UAl_4," *J. Metals*, **3**, (9), 800–02 (1951).

3. N. P. ALLEN, United Kingdom, unpublished information (1947).

4. H. A. SALLER, Battelle Memorial Institute, "Preparation and Properties of Aluminum-Uranium Alloys," TID-65, 9–19 (July, 1948). Classified.

5. V. W. STORHOK and A. A. BAUER, private communication (1958).

6. R. E. RUNDLE and A. S. WILSON, "The Structures of Some Metal Compounds of Uranium" (AECD-2388), *Acta. Cryst.*, **2**, 148–50 (1949).

7. J. T. MASKREY and B. R. T. FROST, "The System Uranium-Lead" (AERE M/R 1027), *J. Inst. Metals* (12), 171–80 (1953).

URANIUM-ANTIMONY

There is evidence of a number of intermetallic compounds in the uranium antimony system.[1–3] The following solubilities of uranium in liquid antimony have been reported [4]:

Temperature, C	650	700	750	800	850	900
Solubility, w/o	0.1	0.3	0.5	0.8	1.8	2.9

CRYSTALLOGRAPHY

The crystallography of USb, U_3Sb_2, and USb_2 compounds is reported by Ferro [1, 2] as shown below.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
USb	Fcc	$a = 6.191$	4				NaCl structure; isomorphous with UN, UP, and UAs
U_3Sb_4	Cubic	$a = 9.095$					
USb_2	Tetragonal	$a = 4.272$ $c = 8.741$					

References

1. R. FERRO, *Atti accad. nazl. Lincei. Rend., Classe sci. fis., mat. e nat.,* **13,** 53-61 (1952).

2. R. FERRO, *Atti accad. nazl. Lincei. Rend., Classe sci. fis., mat. e nat.,* **13,** 151-57 (1952).

3. J. J. KATZ and E. RABINOWITCH, *The Chemistry of Uranium, Part I,* McGraw-Hill Book Company, Inc., New York (1951), pp 241-42.

4. E. E. HAYES and P. GORDON, TID-65, 130-41 (July, 1948). Classified.

URANIUM-ARSENIC

There is evidence supporting three intermetallic compounds in the uranium-arsenic system, but little else is known about these alloys.

CRYSTALLOGRAPHY

The crystallography of UAs and UAs_2 compounds is summarized below. The data for UAs are those of Rundle [1]. Ferro [2] reports that UAs is similar in structure to USb, UN, UP, and UBi.

On the basis of x-ray studies, Iandelli [3, 4] reports the existence of UAs, U_3As_4, and UAs_2.
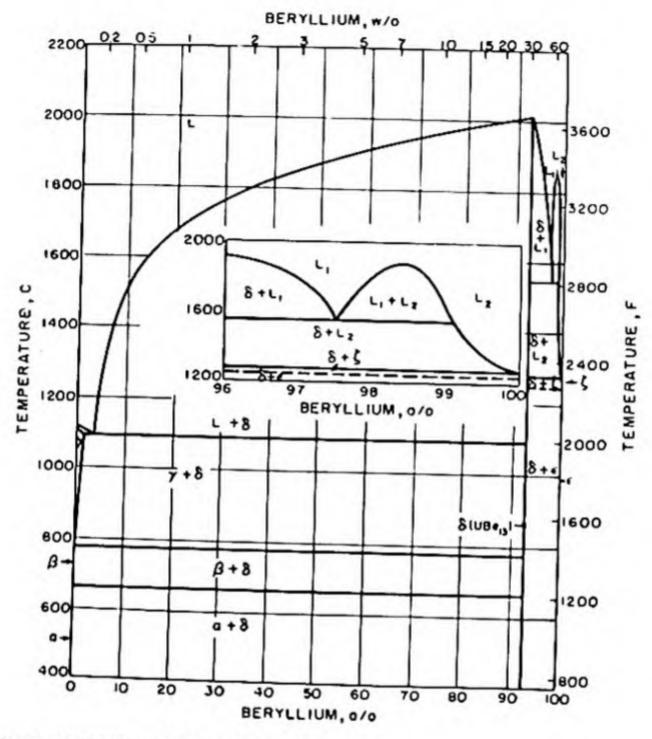
Katz and Rabinowitch [5] have surveyed information on this system.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, Å	Number of molecules	X-ray	Other		
UAs	Fcc	$a = 5.767 \pm 0.01$	4	10.77			NaCl structure, isomorphous with rare-earth arsenides of La, Ce, Pr, Nd
UAs_2	Tetragonal	$a = 3.954$ $c = 8.116$	2	9.8			Isomorphous with UP_2

References

1. R. E. RUNDLE and N. C. BAENZIGER, unpublished information (1944).

2. R. FERRO, *Atti. accad. nazl. Lincei. Rend., Classe sci. fis., mat. e nat.,* **13,** 53-61 (1952).

3. A. IANDELLI, "Uranium Arsenides II. Crystal Structure of UAs_2 and UP_2," *Atti. accad. nazl. Lincei. Rend., Classe sci. fis., mat. e nat.,* **13,** 144-51 (1952).

4. A. IANDELLI, "Uranium Arsenides I," *Atti. accad. nazl. Lincei. Rend., Classe sci. fis., mat. e nat.,* **13,** 138-43 (1952).

5. J. J. KATZ and E. RABINOWITCH, *The Chemistry of Uranium, Part I,* McGraw-Hill Book Company, Inc., New York (1951), pp 241-42.

URANIUM-BERYLLIUM

THE CONSTITUTIONAL DIAGRAM

The diagram shown here is the work of Buzzard and co-workers [1]. It represents the results of much difficult and trying work, since the atomic-weight ratio of uranium to beryllium is very high. The work was further complicated by the high volatility of beryllium at elevated temperatures. In general, the less elaborate work of other investigators is in agreement with this diagram. No confirmation exists for the tentatively proposed high-temperature modification in beryllium, which is designated as zeta (ζ) in the diagram. Details of the monotectic reaction are amplified in the inset of the diagram.

Buzzard reports that the eutectic between uranium and UBe_{13} occurs at a composition of less than 5 a/o beryllium (0.2 w/o). He also reports that the solubility of beryllium in uranium is small and that of the solubility of uranium in beryllium has not been detected.[1]

The National Physical Laboratory reports that the solid solubility of beryllium in uranium is between 2.8 and 8.4 a/o beryllium. The beryllium-rich eutectic contains about 0.06 a/o uranium [4].

CRYSTALLOGRAPHY

Data for UBe_{13} are summarized in the accompanying tabulation [2, 3]. There is no doubt that the unit cell is complex, although first studies tended to indicate a simple cubic structure with a lattice constant of about 5 A. Baenziger and Rundle [2] studied a whole series of MBe_{13} compounds where M was uranium, thorium, cerium, and zirconium. Study of rotation and Weissenberg diagrams of single crystals of $ZrBe_{13}$ revealed the more complex structure. On closer inspection, they found that the (531) reflection, which requires the larger unit, could be seen on powder diagrams. Their data were calculated from back-reflection data obtained with a symmetrical, self-focusing powder camera [2].

Koehler and co-workers [3] studied single crystals of UBe_{13} by both x-ray- and neutron-diffraction methods. Their work is in complete agreement with that of Baenziger and Rundle [2].

Phase	Unit cell			Density, g/cm^3		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta (UBe_{13})	Fcc	$a = 10.2568 \pm 0.0001$	8	4.373	4.420 $\pm$ 0.002 at 26 C	Fm3c	Isomorphous with $NaZn_{13}$, $ThBe_{13}$, $CeBe_{13}$, and $ZrBe_{13}$

References

1. R. W. BUZZARD, J. T. STERLING, E. A. BUZZARD and J. H. DARR (AECD-3417), J. Res. Natl. Bur. Standards, **50**, 63–67 (2), (1953).

2. N. C. BAENZIGER and R. E. RUNDLE, "The MBe_{13} Compounds" (AECD-2506), *Acta Cryst.*, **2**, 258 (1949).
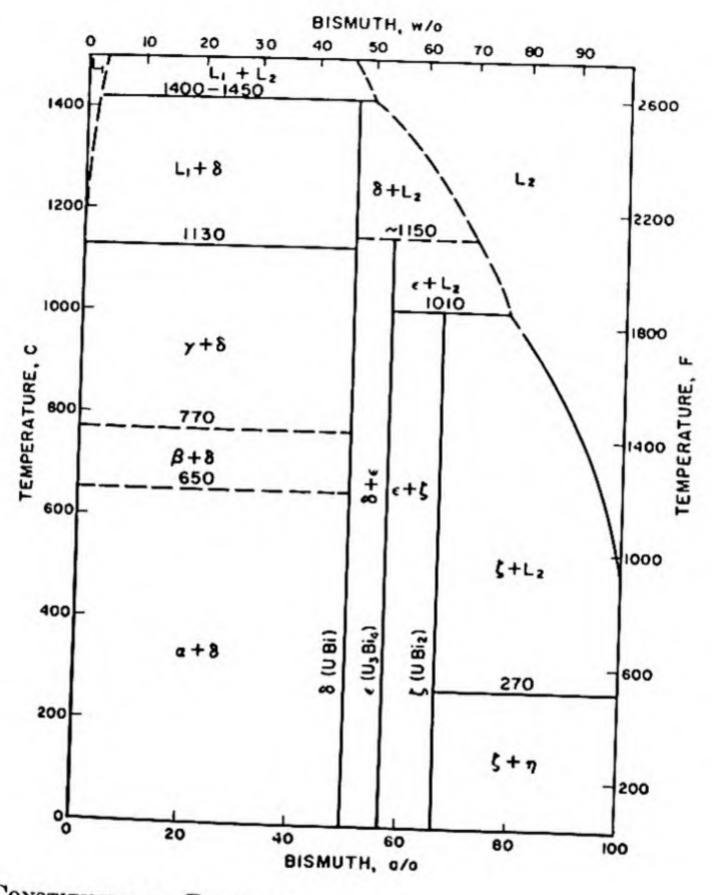
3. W. C. KOEHLER, JOSEPH SINGER and A. S. COFFINBERRY, "X-Ray and Neutron Diffraction Studies of the MBe_{13} Intermetallic Compounds" (AECD-3298), *Acta Cryst.*, **5**, 394 (1952).

4. National Physical Laboratory, United Kingdom, unpublished information (October, 1948).

URANIUM-BISMUTH

The Constitutional Diagram

The original study of the uranium-bismuth system was performed by Ahmann and Baldwin [1]. Their data indicated the existence of two compounds, UBi and UBi_2, and their diagram, although incomplete, had all the major features of the system as it is now interpreted. The work of Teitel [2] and Ferro [3] brought about revision of the system as it is shown here and identified the compounds as UBi, U_3Bi_4, and UBi_2.

Determinations of the solubility of uranium in bismuth by Greenwood [6], who used filtration, by Cotterill [7], who used thermal analysis, and by Bareis [8], who used filtration and flotation techniques, are sub-

stantially in agreement with the diagram as shown. Greenwood [6] found the solubility obeyed the relationship $\log_{10}$ (uranium, w/o) $= 3.00 - (2440/T)$, where T is the absolute temperature, and obtained the following values:

Temperature, C	515	546	602	668	722	760	796	816	898	960
Solubility, w/o	0.7	0.9	1.3	2.7	3.5	5.1	6.7	9.3	13.9	19.6

The values of Bareis [8] agree well with those of Greenwood, but since they cover a different temperature range, the values are given below:

Temperature, C	271	300	350	400	450	500	550	600	650	700
Solubility, w/o	0.031	0.051	0.108	0.21	0.36	0.60	0.97	1.47	2.18	3.1

CRYSTALLOGRAPHY

Data on the crystallography of the intermetallic compounds in this system are summarized in the tabulation below.

The structure of UBi is from the work of Teitel [2] and was determined by means of neutron-diffraction experiments. Both Ferro [3] and Brewer [4] have reported the UBi structure to be face-centered cubic and give lattice constants of $a = 6.356$ A and $a = 6.364$ A, respectively.

The data for U_3Bi_4 and for UBi_2 are from the work of Ferro [3, 5].

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta (UBi)	Be tetragonal	$a = 11.12$ $c = 10.55$	24	13.6			
Epsilon (U₃Bi₄)	Cubic	$a = 9.350$	4	12.59			
Zeta (UBi₂)	Tetragonal	$a = 4.445$ $c = 8.908$	2	12.38		P4/nmm	C38-type structure

References

1. D. H. AHMANN and R. R. BALDWIN, "The Uranium-Bismuth System," CT-2961 (November 12, 1945).

2. R. J. TEITEL, "Uranium-Bismuth System," *Trans. A.I.M.E.*, **209**, 131–36 (1957).

3. RICARDO FERRO, "Alloys of Uranium With Bismuth II," *Atti accad. nazl. Lincei. Rend., Classe sci. fis., mat. e nat.*, **14**, 89–94 (1953).

4. L. BREWER, R. K. EDWARDS and D. H. TEMPLETON, "The Crystal Structure of UBi," AECU-653 (November 15, 1949).

5. RICARDO FERRO, "Alloys of Urnaium With Bismuth," *Atti. accad. nazl. Lincei. Rend., Classe sci. fis., mat. e nat.*, **13**, 401–5 (1952).

6. G. W. GREENWOOD, "The Solubilities of Uranium and Thorium in Liquid Bismuth," A.E.R.E. M/R 2234 (June, 1957).

7. P. COTTERILL, United Kingdom, unpublished information (April, 1957).

8. D. W. BAREIS, "Liquid Reactor Fuels: Bismuth-Uranium System," BNL-75 (September 15, 1950).

URANIUM-BORON

Although the diagram has not been completed some data are available on the general characteristics of the uranium-boron system. The system contains three intermetallic compounds: UB_2, UB_4, and UB_{12} [1]. The portion of the diagram between pure uranium and UB_2 has been studied [2] and determined to be of simple eutectic form with the eutectic temperature between 1120 and 1128 C. The melting point of UB_2 is 2440 C. UB_4 exhibits a higher melting temperature [3] and forms a eutectic with UB_2 well above 1565 C.

The compound UB_{12} is reported to be too unstable for refractory use [3] and it does not exist at as such high temperatures as do UB_2 and UB_4.

CRYSTALLOGRAPHY

The crystallography of UB_2, UB_4, and UB_{12} is summarized below. The lattice constants for UB_2 are reported by Daane and Baenziger [1]. Similar results are reported by Brewer [3], but the lattice constants are given as $a = 3.136 \pm 0.006$ A and $c = 3.988 \pm 0.008$ A.

The lattice constants of UB_4 are taken from the work of Brewer [3]. Similar but slightly lower values are reported by Bertaut [4]. Both Bertaut [4] and Zalkin [5] report the space group of UB_4 to be P4/mbm.

The data for UB_{12} are the work of Andrieux and Blum [6]. Additional discussion of the uranium borides can be found in *The Chemistry of Uranium* [7].

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
UB_2	Hexagonal	$a = 3.12$ $c = 3.96$	1	12.82	12.8		Axial ratio suggests it may be isomorphous with AlB_2
UB_4	Tetragonal	$a = 7.075$ ± 0.004 $c = 3.979$ ± 0.002	4			P4/mbm	Isomorphous with ThB_4 and CeB_4
UB_{12}	Fcc	$a = 7.473$	4	5.825		Fm3m	

References

1. Adrian Daane and N. C. Baenziger, unpublished information (July 18, 1949).

2. B. W. Howlett and B. Marriott, Associated Electrical Industries Research Laboratory, United Kingdom, unpublished information (March, 1957).

3. L. Brewer, D. L. Sawyer, D. H. Templeton and C. H. Dauben, "The Borides of Uranium and Thorium" (AECD-2823), *J. Chem. Phys.*, **18**, 391 (1950).

4. F. Bertaut and P. Blum, "The Structure of the Borides of Uranium," *Compt. rend.*, **229**, 666–67 (1949).

5. A. Zalkin and D. H. Templeton, "The Crystal Structure of CeB₄, ThB₄, and UB₄." *Acta Cryst.*, **6**, 269–272 (1953); *J. Chem. Phys.*, **18**, 391 (1950).

6. J. L. Andrieux and P. Blum, *Compt. rend.*, **229**, 210 (1949).

7. J. J. Katz and E. Rabinowitch, *The Chemistry of Uranium, Part I*, McGraw-Hill Book Company, Inc., New York (1951), p 214.

URANIUM-CALCIUM

There are very few data on the uranium-calcium system. However, in attempts to prepare calcium alloys, Ahmann [1] found no reaction between uranium and calcium after as much as 24 hr at 800 C.

CRYSTALLOGRAPHY

There are no compounds in the uranium-calcium system.

Reference
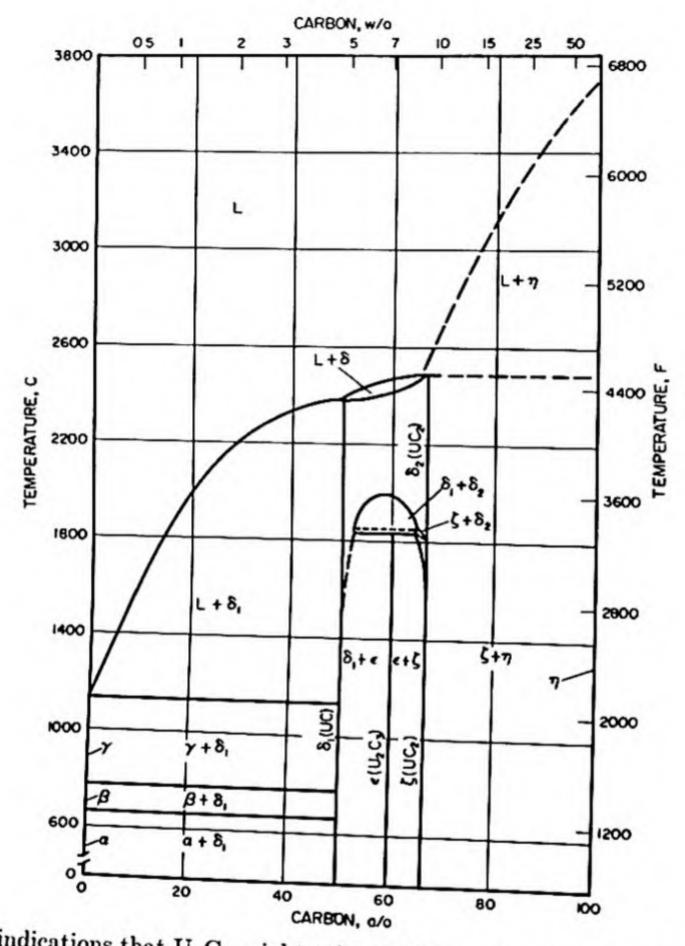
1. D. H. Ahmann, "Note on Attempts to Prepare Magnesium and Calcium Alloys of Uranium," CT-2959 (December 5, 1945).

URANIUM-CARBON

THE CONSTITUTIONAL DIAGRAM

The constitutional diagram for uranium-carbon shown in the accompanying figure [1] has been revised to show the allotropic transformation of UC_2 from tetragonal to face-centered cubic at 1820 ± 20 C [2]. Two additional compounds, UC and U_2C_3, are found in the system. Early investigators [3] did not discover U_2C_3 by x-ray examination but had in-

direct indications that U_2C_3 might exist at high temperatures and decompose during cooling. Later, Mallett and co-workers [4] obtained the sesquicarbide by heating the proper uranium-carbon composition in the range 1250 to 1800 C and then subjecting it to a slight stress. The requirement of residual stress for the formation of U_2C_3 has since been confirmed [2]. The sesquicarbide formed by this technique is stable from room temperature to 1840 ± 20 C.

UC and UC_2 are reported to be mutually soluble in the region above the sesquicarbide [1, 2].

Solubilities of carbon in gamma uranium have been reported by Blumenthal [5] as follows:

Temperature, C	Solubility, ppm
800	65
950	70
975	80
1000	90
1020	110
1050	115

CRYSTALLOGRAPHY

The crystallography of the uranium carbides is summarized in the tabulation below. The data for UC are from Rundle [6]. Wilson [2] gives values of 4.9614 and 4.9597 ± 0.0005 A for UC at room temperature, and Litz [7] reports a value of $a = 4.955$ A. The data for U_2C_3 are from Mallett [4]; a value of 0.8070 ± 0.0005 A is given by Wilson [2]. The data for the tetragonal and face-centered cubic forms of UC_2 are from Wilson. Similar data are reported by Rundle [6], who reports values of $a = 3.524$ and $c = 5.999$, and by Litz [7] who gives lattice constants of $a = 3.54$ and $c = 5.99$ A.

Discussion of this system can also be found in *The Chemistry of Uranium* [8].

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta₁ (UC)	Fcc	$a = 4.961$	4	13.63			NaCl-type structure
Epsilon (U_2C_3)	Cubic	$a = 8.088$	8	12.88		I43d	CaC₂-type structure
Zeta (UC_2)	Bc tetragonal	$a = 3.516$ $c = 5.972$	2	11.68		I4/mmm	CaC₂-type structure
Delta₂ (UC_2)	Fcc	$a = 5.472$	4				CaF₂-type structure; data for 1820 C

References

1. M. W. MALLETT, A. F. GERDS and H. R. NELSON, "The Uranium-Carbon System," *Trans. Electrochem. Soc.*, **99**, 197–204 (1952).

2. W. B. WILSON, private communication (1957).

3. H. A. WILHELM, P. CHIOTTI, A. I. SNOW and A. H. DAANE, "The Carbides of Uranium and Thorium," *J. Chem. Soc.* (Supplementary Issue 2), 318–321 (1949).

4. M. W. MALLETT, A. F. GERDS and D. A. VAUGHAN, "Uranium Sesquicarbide" (AECD-3060); *Trans. Electrochem. Soc.*, **98**, 505–09 (1951).

5. B. BLUMENTHAL, "Uranium Alloy Newsletter," WASH-296, 10 (March, 1956).

6. R. E. RUNDLE, N. C. BAENZIGER, A. S. WILSON and R. A. McDONALD, "The Structures of the Carbides, Nitrides, and Oxides of Uranium," *J. Am. Chem. Soc.*, **70**, 99–05 (1948).

7. L. LITZ, A. B. GARRETT and F. C. CROXTON, "Preparation and Structure of the Carbides of Uranium," *J. Am. Chem. Soc.*, **70**, 1718 (1948).

8. J. J. KATZ and E. RABINOWITCH, *The Chemistry of Uranium, Part I,* McGraw-Hill Book Company, Inc. (1951), p. 217.

URANIUM-CERIUM

Only limited data exist for the uranium-cerium system.

Uranium and cerium are only partially miscible in the liquid state. [1, 2, 3, 4] There is evidence of a eutectic at the uranium end of the system, perhaps at about 1000 C.[2, 3] The solubility of cerium in liquid uranium is reported to increase from 1.0 w/o at 1150 C to 1.5 w/o at 1250 C, while the solubility of uranium in cerium increases from 1.3 w/o at 1000 C to 3.5 w/o at 1250 C.[4]

CRYSTALLOGRAPHY

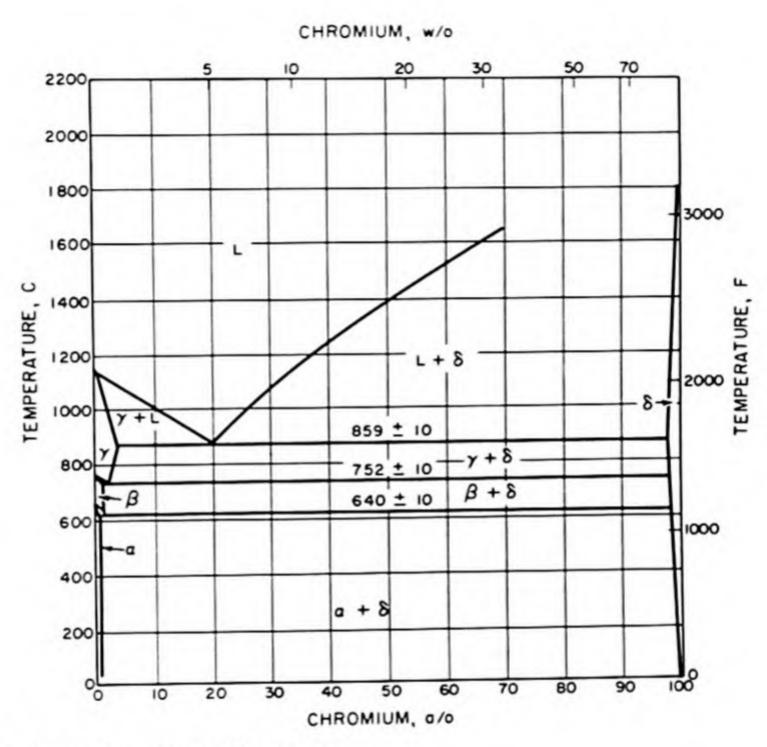There are no compounds in the uranium-cerium system.

References

1. National Physical Laboratory, United Kingdom, unpublished information (May, 1949).

2. M. NEHER, B. D. CULLITY and A. R. KAUFFMAN, unpublished information (January, 1945).

3. A. B. GRENINGER and F. FOOTE, unpublished information (May, 1945).

4. H. A. WILHELM, Nuclear Fuels Newsletter, WASH-704 (December, 1952). Classified.

URANIUM-CHROMIUM

THE CONSTITUTIONAL DIAGRAM

Chromium is one of the few elements which forms a eutectic with uranium, without intervening intermetallic compounds. The diagram which is shown here is based largely on the work of Daane and Wilson [1], who studied the system by x-ray, thermal, and metallographic techniques. The eutectoid isotherms were revised by Saller, on the basis of both thermal and dilatometric measurements. The eutectic composition appears to be slightly less than 20 a/o chromium, or about 19.4 a/o chromium [2]. This composition was determined by using a series of low-carbon cast samples. The work of Mott and Haines [3] confirms the diagram presented here.

The solubility of uranium in chromium is slight, and the solubility of chromium in uranium is limited [1]. In the gamma uranium, the solubility of chromium is variously reported to be 4 a/o [1] and greater than 5 a/o [3].

On the basis of the behavior of beta-treated alloys during isothermal transformation in the alpha region [4], the solubility in beta-uranium is estimated to be about 1.5 a/o chromium. The solubility of chromium in alpha-uranium is somewhat less than in the beta, but is not known [1, 3].

Bloom and Grant [5] have reported that an allotropic change occurs in chromium just below its melting point, but this change is not confirmed by McCaldin and Duwez [6]. In either case, this portion of the diagram would be relatively unimportant for working with these alloys.

CRYSTALLOGRAPHY

There is no compound in the uranium-chromium system.

References

1. A. H. DAANE and A. S. WILSON, "Uranium-Chromium System," *J. Metals,* 7, 1219 (1955).

2. H. A. SALLER, F. A. ROUGH and R. F. DICKERSON, "Preparation and Properties of the Eutectic Uranium-Chromium Alloy," BMI-884 (November, 1953).

3. B. W. MOTT and H. R. HAINES, "A Metallographic Study of the Transformation of Beta, etc." (Appendix I: Note on the Constitution of U-Cr Alloys), AERE M/R 1211 (June 19, 1953).

4. D. W. WHITE, Knolls Atomic Power Laboratory, unpublished information (1952).

5. D. S. BLOOM and N. J. GRANT, "Chromium-Nickel Phase Diagram," *J. Metals,* (11), 1009 (1951).

6. J. A. McCALDIN and POL DUWEZ, "Allotropic Transformations at High Temperature," *J. Metals,* (5), 619–20 (1954).
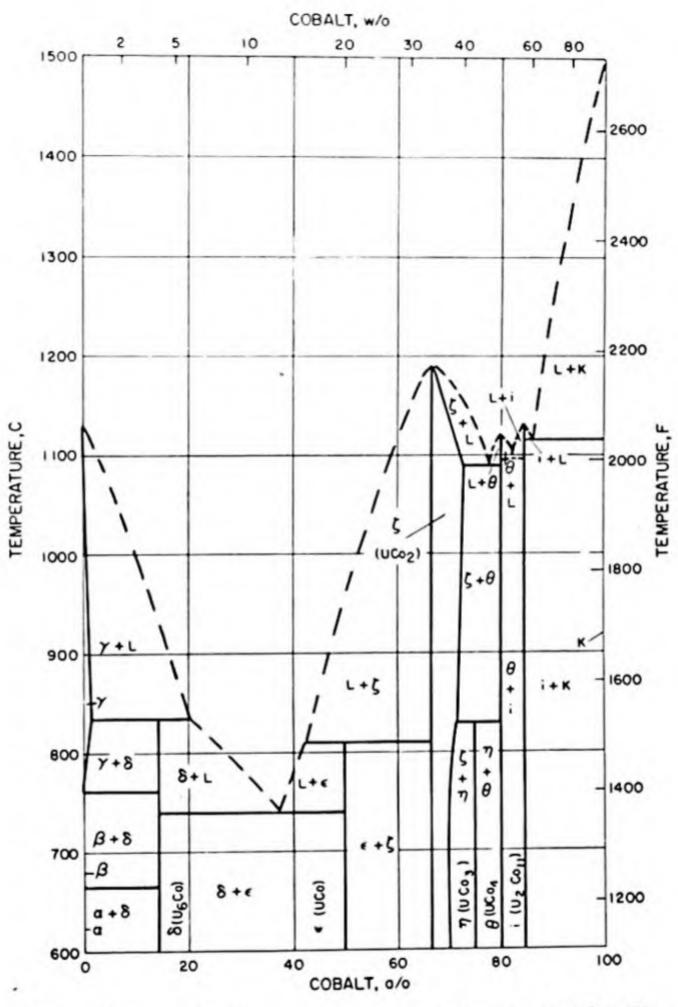
URANIUM-COBALT

THE CONSTITUTIONAL DIAGRAM

The following diagram shown is that of Waldron and Browne [1] and is in agreement with the earlier work of Noyce and Daane [2] except at the cobalt-rich end, where Waldron and Browne report a larger solubility range for UCo_2 and three additional compounds with compositions UCo_3, UCo_4, and U_2Co_{11}.

CRYSTALLOGRAPHY

The crystal structures are known for three of the six compounds [3]. The compound U_6Co is isomorphous with U_6Mn, U_6Fe, and U_6Ni. The observed unit-cell volume for all these phases is nearly equal to the volume

calculated by addition of atomic volumes, or about 550 A^3. The atomic positions can be described on the basis of space group I4/mcm, although a possible variation from their positions in space groups I42 and $\bar{I}4c2$ has not been eliminated.

The structure of UCo_2 has been reported by both Baenziger [3] and Waldron and Browne, the latter claiming a large variation of unit cell size with composition. UCo_2 has the C15, $MgCu_2$ structure and is isomorphous with UFe_2 and UMn_2 but not with UNi_2, which has the C14,

MgZn$_2$ structure. Ternary alloys involving these phases are reported in the section devoted to ternary alloys.

Crystal structures have not yet been reported for the remaining phases.

| Phase | Unit cell | | | Density, g/cm^3 | | Space group | Remarks |
	Type	Dimensions, Å	Number of molecules	X-ray	Other		
Delta (U_6Co)	Bc tetragonal	10.36 ± 0.02 5.21 ± 0.02	4	17.7		I4/mcm I42 or I4c2	Isomorphous with U_6Mn, U_6Fe, and U_6Mn
Epsilon (UCo)	Bcc	6.3557 ± 0.0004	8	15.37		I43m or I2, 3	
Zeta (UCo_2)	Fcc	6.929 to 7.000	8	13.83		Fd3m	C15, MgCu$_2$ structure; isomorphous with UFe$_2$ and UMn$_2$

References
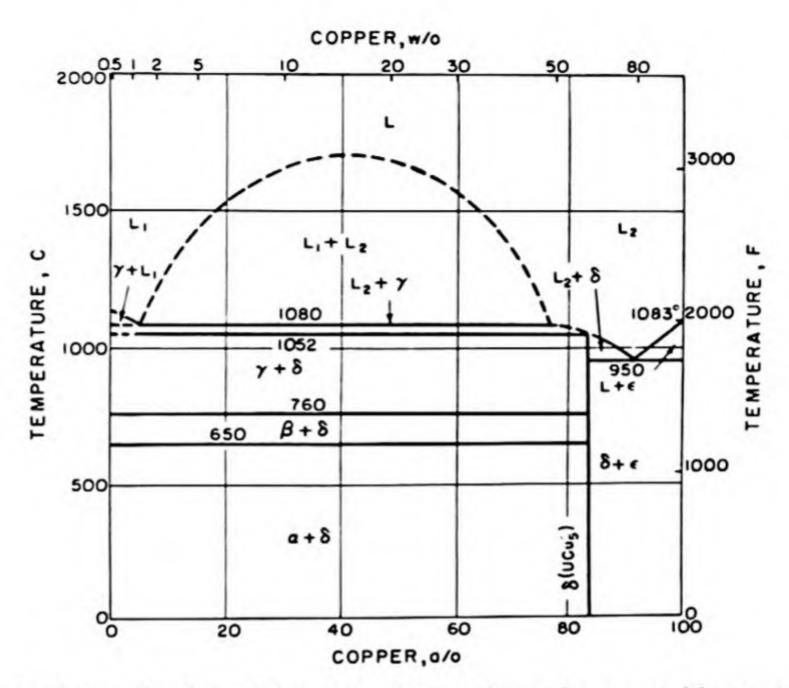
1. M. B. Waldron and J. D. Browne, United Kingdom, unpublished information (1956).

2. W. K. Noyce and A. H. Daane, "The Uranium-Cobalt System," AECD-2826 (March 1, 1946).

3. N. C. Baenziger, et al., "Compounds of Uranium With the Transition Metals of the First Long Period" (AECD-2598), *Acta Cryst.*, 3, 34–40 (1950).

URANIUM-COPPER

THE CONSTITUTIONAL DIAGRAM

The system uranium-copper has been studied and a diagram has been constructed on the basis of information obtained by x-ray diffraction, thermal analysis, and metallography [1]. The diagram is self explanatory. The region of immiscibility above 1080 C is reported to extend from 1.5 to 48 w/o copper. The immiscibility was found to exist in 5 and 45 w/o copper alloys at 1550 C and in a 25 w/o copper alloy at 1850 to 1900 C [1].

Data from the United Kingdom [2, 3] indicate that an additional compound, or compounds, may occur in this system. This indication is not supported by the work of Wilhelm and Carlson [1], although a small thermal break was observed at 860 C in the uranium-rich portion of the system. This break conceivably could be related to the presence of an additional compound, although it was considered to be the result of con-

COPPER, w/o

tamination at the time of the study. If an additional compound is present in the system, it is surely in the high-uranium region, since x-ray studies showed that UCu_5 and copper exist together in copper-rich alloys [1].

There is evidence of slight solubility of uranium in UCu_5. There is no evidence of appreciable solubility of uranium in copper, or of copper in uranium [1].

CRYSTALLOGRAPHY

The structure of UCu_5 has been determined by Baenziger [4]. The data on this compound are tabulated below. The dimensions of the face-centered cubic unit cell vary from 7.033 ± 0.002 to 7.038 ± 0.001 A, indicating a slight solubility of uranium in UCu_5.

Wilhelm and Carlson [1] have reported a lattice constant of

$$a = 7.0208 \pm 0.002 \text{ A.}$$

The calculated and observed densities are 10.60 ± 0.02 and 10.6 g/cm^3, respectively.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta (UCu₅)	Fcc	7.033 ± 0.002 to 7.038 ± 0.001	4			F$\bar{4}$3m or F23	Isomorphous with UNi₅, PdBe₅, and AuBe₅

References

1. H. A. WILHELM and O. N. CARLSON, "The Uranium-Manganese and Uranium-Copper Alloy Systems" (AECD-2717), *Trans. Am. Soc. Metals*, **42**, 1311 (1950).

2. Fulmer Research Institute, United Kingdom, unpublished information (1952–1953).

3. Swansea University College, United Kingdom, unpublished information (May, 1951).

4. N. C. BAENZIGER, R. E. RUNDLE, A. I. SNOW and A. S. WILSON, "Compounds of Uranium With the Transition Metals of the First Long Period" (AECD-2598), *Acta Cryst.*, **3**, 34–40 (1950).

URANIUM-DYSPROSIUM

Uranium and dysprosium exhibit an immiscibility gap in the liquid state. Solubility of dysprosium in liquid uranium is reported to increase from 0.15 w/o at 1150 C to 0.2 w/o at 1250 C [1].

CRYSTALLOGRAPHY

Nothing is known concerning the possibility of compounds in this system.

Reference

1. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.

URANIUM-ERBIUM

Uranium and erbium exhibit an immiscibility gap in the liquid state. Solubility of erbium in liquid uranium is reported to increase from 0.15 w/o at 1150 C to 0.2 w/o at 1250 C. [1]

CRYSTALLOGRAPHY

Nothing is known concerning the possibility of compounds in this system.

Reference

1. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.

URANIUM-EUROPIUM

Uranium and europium show little miscibility in the liquid state. The solubility of europium in liquid uranium is reported to be 0.15 w/o at 1150 C and 0.2 w/o at 1250 C, while uranium solubility in europium is given as 0.5 w/o at 1000 C and 1.3 w/o at 1250 C.[1]

CRYSTALLOGRAPHY

Data concerning the possibility of compounds in this system are not available.

Reference

1. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.

URANIUM-GADOLINIUM

Uranium and gadolinium exhibit an immiscibility gap in the liquid state. Solubility of gadolinium in liquid uranium is reported to increase from 0.075 w/o at 1150 C to 0.15 w/o at 1250 C.[1]

CRYSTALLOGRAPHY

Nothing is known concerning the possibility of compounds in this system.

Reference
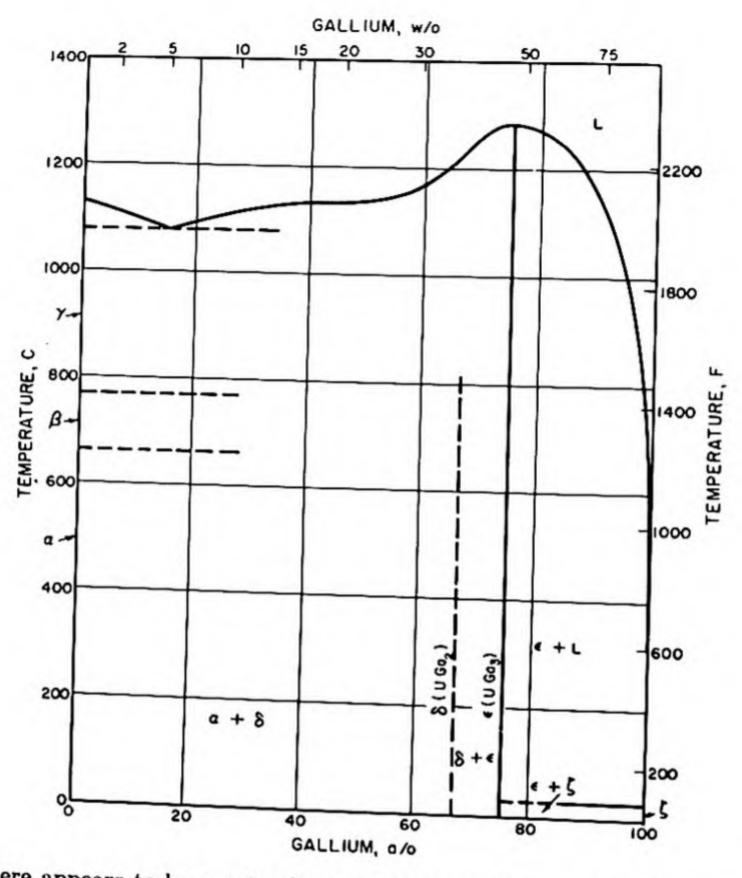
1. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.

URANIUM-GALLIUM

THE CONSTITUTIONAL DIAGRAM

The liquidus of the system has been determined by Jaffee. [1] In addition, evidence of two compounds has been reported. Maskrey and Frost [2] reported UGa_3, while Dempster [3] reported UGa_2. Because work in the United Kingdom [4] tends to support the presence of the second compound, it is included with the other data to give a tentative diagram.

Judging from the liquidus and a reported melting point of about 1300 C for UGa_3 [4], it seems likely that UGa_3 melts congruently. The compound UGa_2, if present, may be stable to some lower temperature.

There appears to be a eutectic at the high-uranium end of the system where a dip in the liquidus occurs. Jaffee [1] found little solubility of uranium in solid gallium. He found the melting point of gallium virtually unaffected by small additions of uranium. On the other hand, it was reported from the United Kingdom that a eutectic occurs at 14 a/o uranium and about 28 C [4]. This report is in serious disagreement with the liquidus as shown. Since complete information is not available, a full evaluation cannot be made.

Jaffee's method for determining the liquidus was rather simple; he determined solubility by feeling with a stirring rod to determine whether uranium was present in the bottom of a crucible of gallium [1]. In spite of the simplicity of his method, the resulting data connect nicely with fil-

tration data obtained by Hayes [5] and Wilkinson [6] for temperatures of 700 and 500 C at the gallium end of the system.

The solid solubility of gallium in uranium is reported to be very low [6].

CRYSTALLOGRAPHY

The data for UGa_3 shown in the tabulation below are from the work of Frost and Maskrey [2]. Iandelli has also reported UGa_3, giving a lattice constant $a = 4.249$ A [7]. UGa_2 data reported by Dempster [3] were not available.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
UGa₂	No data available						
UGa₃	Simple cubic	$a = 4.2475$	1	9.686		Pm3m	L12-type, AuCu₃ ordered structure; isomorphous with UAl₃, USn₃, UIn₃, USi₃, UGe₃, UPb₃

References

1. R. I. JAFFEE, R. M. EVANS, E. O. FROMM and B. W. GONSER, "Gallium in Nuclear Reactors; Considerations for Use in Liquid Fuel Rods," BMI-T-20 (January, 1950). Classified.

2. J. T. MASKREY and B. R. T. FROST, "The System Uranium-Lead" (AERE M/R 1027), *J. Inst. Metals*, (12), 171–80 (1953).

3. A. J. DEMPSTER, Progress Report, AL-4120, (March, 1948).

4. Atomic Energy Research Establishment, United Kingdom, unpublished information (May, 1951).

5. E. E. HAYES and P. GORDON, *J. Met. and Cer.*, TID-65, 130–141 (July, 1948). Classified.

6. WILKINSON, unpublished information (March, 1948).

7. A. IANDELLI and R. FERRO, *Ann. chim.* (Rome), **42**, 598–606 (1952).

URANIUM-GERMANIUM

No information is available on the constitution of the uranium-germanium alloys, except that a compound, UGe_3, has been identified [1, 2].

CRYSTALLOGRAPHY

The crystallography of UGe_3, as reported by Maskrey and Frost [2], is shown below. Iandelli [1] reports a value of $a = 4.198$ A for UGe_3, and reports UGa_3, UIn_3, UTl_3, USi_3, and UPb_3 to have similar structures.

Phase	Unit cell			Density, g·cm³		Space group	Remarks
	Type	Dimensions, Å	Number of molecules	X-ray	Other		
UGe₃	Simple cubic	$a = 4.2062$	1			Pm3m	L12-type structure, isomorphous with UAl₃, USn₃, USi₃, UGa₃, UIn₃, UPb₃
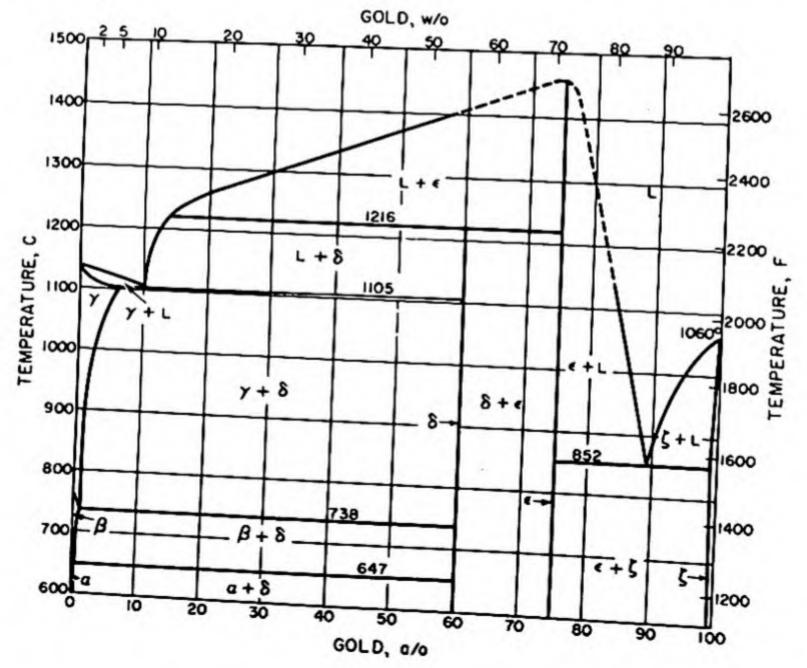
References

1. ALDO IANDELLI and RICARDO FERRO, *Ann. chim.* (Rome), **42**, 598–606 (1952).

2. J. T. MASKREY and B. R. T. FROST, "The System Uranium-Lead" (AERE M/R 1027), *J. Inst. Metals*, **811**, 171–180 (December, 1953).

URANIUM-GOLD

THE CONSTITUTIONAL DIAGRAM

The uranium-gold system has been studied by Buzzard [1]. The diagram shown was constructed from data obtained by thermal, microscopic, and x-ray analyses.

The uranium-rich eutectic is reported to occur at 1105 C and 10.5 a/o gold. The gold-rich eutectic is reported to occur at 87.5 a/o gold and 852 C.[1]

Two compounds were identified by Buzzard, although the structures have not been determined. The compounds appear to be delta (U_2Au_3) and epsilon (UAu_3).[1]

The solubility of uranium in gold appears to be between 0.2 and 0.3 a/o at 852 C, while the solubility of gold in uranium is approximately 6 a/o at 1105 C.[1]

Additions of gold lower the transformation temperatures of uranium to 738 and 647 C, as shown in the diagram [1].

Data from the United Kingdom do not agree well with this diagram. The National Physical Laboratory reports that as many as six compounds may be present in the system.[2] The completeness of the diagram by Buzzard and the apparent agreement of data obtained by x-ray diffraction, thermal analysis, and metallographic examination lend strong support to the diagram shown.

CRYSTALLOGRAPHY

No information is available on the crystal structure of the compounds in the uranium-gold system.

References

1. R. W. BUZZARD and J. J. PARK, "The Gold-Uranium System," *J. Natl. Bur. Standards*, **53**, 291 (1954).

2. National Physical Labora tory, "Note on Some Alloys of Gold and Uranium," AERE X/M 100 (1952)·

URANIUM-HOLMIUM

Uranium and holmium exhibit an immiscibility gap in the liquid state. Solubility of holmium in liquid uranium is reported to increase from 0.025 w/o at 1150 C to 0.075 w/o at 1250 C.[1]
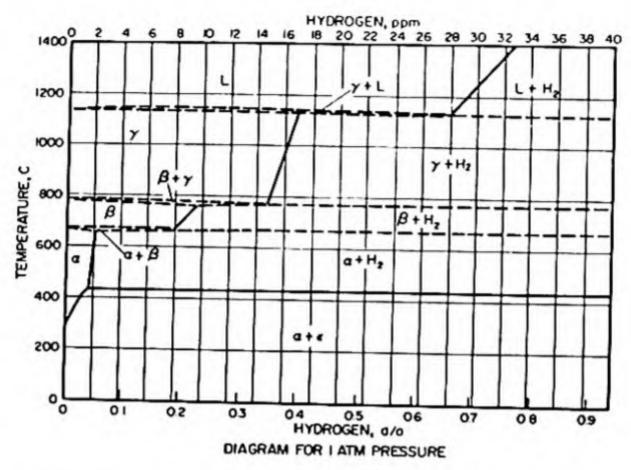
CRYSTALLOGRAPHY

Nothing is known concerning the possibility of compounds in this system.

Reference
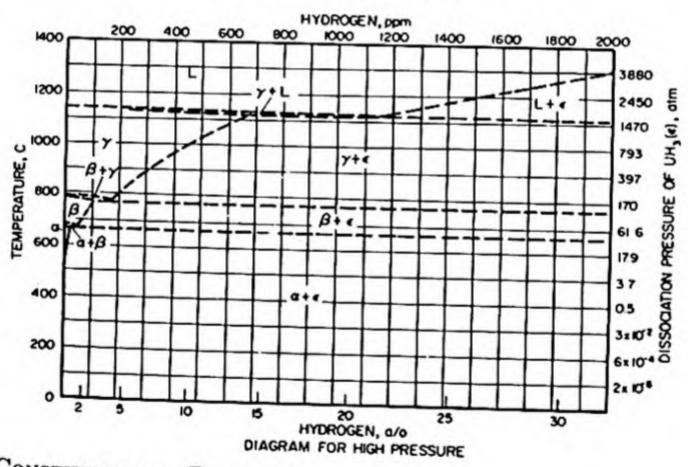
1. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.

URANIUM-HYDROGEN

DIAGRAM FOR 1 ATM PRESSURE

DIAGRAM FOR HIGH PRESSURE

THE CONSTITUTIONAL DIAGRAM

The uranium-hydrogen system has received considerable study. Diagrams illustrating the solubility of hydrogen in uranium at 1-atm pressure and at high pressure have been determined and are shown.[1] Work done since the diagrams were developed has shown that the diagrams are useful; the data are reproducible by the original techniques.

The data were determined by an absorption technique. In this process a sample of uranium rod, dry abraded under argon, is introduced into a

gasometric apparatus which is evacuated and then filled with a measured amount of hydrogen. The amount of hydrogen absorbed is calculated from pressure changes in a known volume. The precision of the method is ± 0.2 ppm for a 25-g sample [1].

Mattraw [2] reports a solubility of 3.0 ppm at 295 C and 100-μ pressure. These data disagree with those of Mallett [1] by a factor of 250. However, it is probable that Mattraw had not observed true interstitial solution of hydrogen, but rather chemisorption on the surface of his finely divided sample. Samples of small surface-to-mass ratio do not show the anomalous high hydrogen pickup.[1]

Many people have contributed to the present knowledge of UH_3, the only hydride in this system. It has been shown that UH_3 exists in two crystallographic forms.[3, 4] Delta UH_3 (called "alpha" UH_3 by Mulford), the more recently discovered form, has been produced by reacting uranium powder with hydrogen gas at 25 to minus 80 C [3], by reacting massive uranium with hydrogen gas at minus 40 C, and by electrolysis of a solution of $HClO_4$ or Na_2CO_3, where uranium is used as the cathode [4]. Mulford suggests that delta is metastable. The yield of delta increases as the temperature of formation is decreased.[3]

Once formed, delta does not decompose during annealing at 100 C but does decompose at 250 C. No attempt was made to show the delta phase in the diagram because epsilon ("beta" UH_3) is the phase commonly observed.

CRYSTALLOGRAPHY

Uranium hydride has been shown to exist in two forms. Data for both delta and epsilon are given in the tabulation along with data for epsilon ("beta") UD_3.

The data for delta UH_3 are from Mulford [3]. Caillat [4] has confirmed this information. He reports that $a = 4.161 \pm 0.002$ A and density is 11.1 g/cm^3.

The data for epsilon UH_3 and epsilon UD_3 are from Rundle.[5, 6] These compounds were studied by x-ray, although the structure was resolved through neutron-diffraction studies of epsilon UD_3. The epsilon UH_3 reported by Rundle was prepared under a pressure of 1800 psi at 500 to 600 C.[6] Hydride prepared at lower pressures yielded lattice constants of $a = 6.32 \pm 0.001$ A. Slightly higher values were obtained in earlier work [7, 8].

The hydrogen atoms in epsilon UH_3 are reported to lie in distorted tetrahedra, equidistant from four uranium atoms with uranium-hydrogen distances of 2.32 A. There are two types of structures, each with 12 nearest hydrogen atoms at this distance. The proposed space group is Pm3n, with parameters for 24 (k) of $y = 0.155 \pm 0.02$ and $Z = 0.31 \pm 0.02$.

These values are sufficiently close to $y = 0.156$ and $Z = 0.313$ to put each hydrogen atom equidistant from four uranium atoms. The structure gives satisfactory agreement between calculated and observed intensities.[5]

The structure of epsilon UH_3 is unique and is not entirely understood, but it is reported that no metallic uranium-uranium bonds of importance are present in the structure. The hydride is assumed to be held together by uranium-hydrogen interactions. Rundle suggests that these interactions may be described in terms of delocalized covalent bonds.[6]

The work of Gibb [9] may be of general interest.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, Å	Number of molecules	X-ray	Other		
Delta ("alpha") UH_3	Cubic	$a = 4.160 \pm 0.001$	2			Pm3n	
Epsilon ("beta") UH_3	Cubic	$a = 6.6310 \pm 0.0008$	8	10.92	10.95	Pm3n	
Epsilon ("beta") UD_3	Cubic	$a = 6.620 \pm 0.002$	8	11.11		Pm3n	

References

1. M. W. MALLETT and M. J. TRZECIAK, "Hydrogen Uranium Relationships," *Trans. ASM*, 50 (1958).

2. H. C. MATTRAW, *J. Phys. Chem.*, 59, 93 (1955).

3. R. N. R. MULFORD, F. H. ELLINGER and W. H. ZACHARIASEN (AECU-2700), *J. Am. Chem. Soc.*, 76, 297–98 (1954).

4. R. CAILLAT, H. CORIOU and P. PERIO, "A New Form of the Hydride of Uranium," *Compt. rend.*, 237, 812–13 (October 12, 1953).

5. R. E. RUNDLE, "The Hydrogen Positions in Uranium Hydride by Neutron Diffraction," (AECD-3111), *J. Am. Chem. Soc.*, 73, 4172–4 (1951).

6. R. E. RUNDLE, "The Structure of Uranium Hydride and Deuteride," *J. Am. Chem. Soc.*, 69 (7), 1719–23 (1947).

7. J. J. KATZ and EUGENE RABINOWITCH, *The Chemistry of Uranium, Part I*, McGraw-Hill Book Company, Inc., New York (1951), pp 180–213.

8. W. H. ZACHARIASEN, unpublished information (1943).

9. THOMAS GIBB, JR., et al., "Metal-Hydrogen Systems III. The Uranium-Hydrogen System," *J. Am. Chem. Soc.*, 74 (12), 6203–07 (1952).

URANIUM-INDIUM

A compound, UIn_3, has been identified.[1, 2] Solubilities of uranium in liquid indium have been reported [3] as given below:

Temperature, C	600	650	700	750	800	850	900
Solubility, w/o	0.08	0.10	0.15	0.25	0.45	0.70	1.05

CRYSTALLOGRAPHY

An intermetallic compound, UIn_3, has been reported.[1, 2] Data for UIn_3 are summarized below [2]. Iandelli [1] reports the same structure, but gives a slightly lower lattice constant, $a = 4.588$ A. He has studied the following UX_3-type compounds: UIn_3, UGa_3, UTl_3, USi_3, UGe_3, and UPb_3.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
UIn_3	Fcc	$a = 4.6013$	1			Pm3m	L12-type structure, isomorphous with UGa_3, USi_3, UGe_3, UPb_3, USn_3, and UAl_3

References

1. ALDO IANDELLI and RICARDO FERRO, *Ann. chim.* (Rome), **42**, 598-60 (1952).

2. J. T. MASKREY and B. R. T. FROST, "The System Uranium-Lead" (AERE M/R-1027), *J. Inst. Metals*, **81**, 171-80 (December, 1953).

3. E. E. HAYES and P. GORDON, *J. Met. and Cer.*, TID-65, 130-41 (July, 1948).

URANIUM-IRIDIUM

The solubility of iridium in uranium at 890 C is reported [1] to be about 3 a/o. A compound, UIr_2, has been identified.

CRYSTALLOGRAPHY
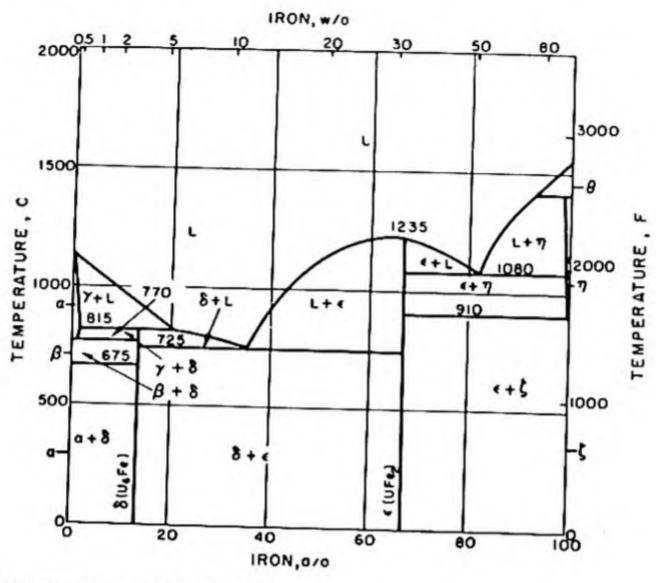
An intermetallic compound, UIr_2, has been reported [2]. It has the Cl5, $MgCu_2$ structure.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
UIr_2	Fcc	$a = 7.509$	8	19.62		Fd3m	C15, $MgCu_2$ structure

References

1. J. J. PARK, private communication (October, 1956).

2. T. J. HEAL and G. I. WILLIAMS, "Compounds of Uranium With the Transition Metals of the Second and Third Long Periods." *Acta Cryst.*, **8**, 494 (1955).

URANIUM-IRON

THE CONSTITUTIONAL DIAGRAM

The uranium-iron diagram has been determined independently by Kauf-
mann [1] and by Grogan [2] and has been studied by Foote [3]. The dia-
gram shown is Kaufmann's. The liquidus points and the isotherms re-
ported by Grogan vary slightly from those of this diagram; otherwise,
the two diagrams are identical.

Grogan [2] reports some details of the uranium-rich alloys. Solubilities
of iron in uranium taken from this work are tabulated below.

Phase	Temperature	Solubility, w/o
Alpha	660 C Alpha-beta isotherm	Nil <0.02 iron
Beta	Alpha-beta isotherm Beta-gamma isotherm	<0.02 iron 0.1 iron
Gamma	Beta-gamma isotherm U₆Fe peritectic	0.2 iron 0.35 iron

The solubility in the gamma region depicted in the accompanying dia-
gram [1] agrees well with the data above.

CRYSTALLOGRAPHY

The structure of U_6Fe has been determined by Baenziger [4] and is isomorphous with U_6Mn, U_6Co, and U_6Ni. The observed unit-cell volume for U_6Fe (557 A^3) is quite close to the volume calculated by assuming additivity of atomic volumes (547 A^3).

The data tabulated for UFe_2 are from the work of Grogan [2]. Kaufmann [1] has reported a slightly higher value for the lattice, $a = 7.050$ A. Similar data have been reported by Baenziger [4] and Brook [5], indicating that UFe_2, UMn_2, and UCo_2 are isomorphous and are the C15-type $MgCu_2$ structure. The compound UNi_2 is reported to have the C14-type $MgZn_2$ structure. Ternary alloys involving all of these phases are described in the section devoted to ternary alloys.

| Phase | Unit cell | | | Density, g/cm³ | | Space group | Remarks |
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta (U_6Fe)	Bc tetragonal	a = 10.31 ± 0.04 c = 5.24 ± 0.02	4	17.7		I4/mcm, I42, or I4c2	Isomorphous with U_6Mn, U_6Co, U_6Ni
Epsilon (UFe_2)	Fcc	a = 7.042	8	13.21		Fd3m	C15-type, $MgCu_2$ structure isomorphous with UAl_2

References

1. P. GORDON and A. R. KAUFMANN, "The Alloy Systems Uranium-Aluminum and Uranium-Iron" (AECD-2683), *J. Metals*, 2 (1), 182 (1950).

2. J. D. GROGAN, "The Uranium-Iron System," *J. Inst. Metals*, 77, 571–80 (1950).

3. FRANK FOOTE, unpublished information (1945).

4. N. C. BAENZIGER, R. E. RUNDLE, A. I. SNOW and A. S. WILSON, "Compounds of Uranium With the Transition Metals of the First Long Period" (AECD-2598), *Acta Cryst.*, 3, 34–40 (1950).

5. G. B. BROOK, G. I. WILLIAMS and E. M. SMITH, "Pseudo-Binary Phase Sections Between Laves Phases in Ternary Alloys of Uranium," *J. Inst. Metals*, 83, 271 (1954–1955).

URANIUM-LANTHANUM

Uranium and lanthanum show little miscibility in the liquid state.[1, 2] The solubility of lanthanum in liquid uranium is reported to be 0.75 w/o at 1150 C and 0.90 w/o at 1250 C, while uranium solubility in lanthanum is given as 0.3 w/o at 1000 C and 1.0 w/o at 1250 C.[1]
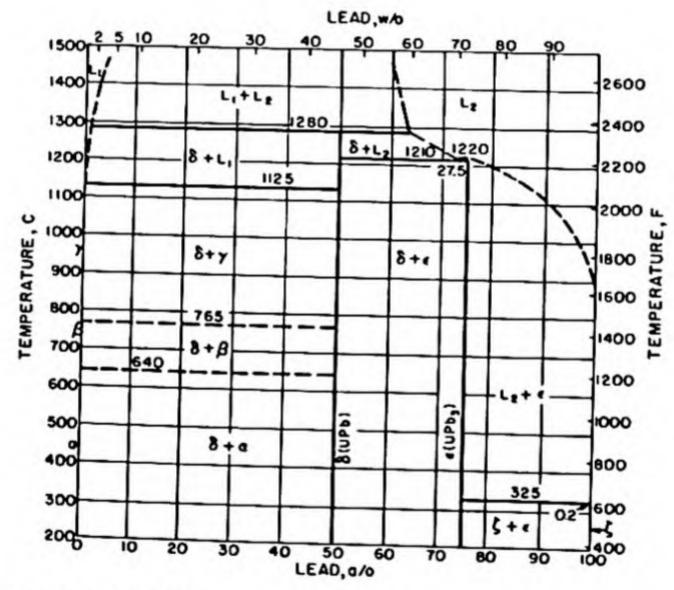
CRYSTALLOGRAPHY

Data concerning the possibility of compounds in this system are not available.

References

1. H. A. WILHELM, "Nuclear Fuels Newsletter." WASH-704 (December, 1957). Classified.
2. National Physical Laboratory, United Kingdom, unpublished information (1949-1950).

URANIUM-LEAD

THE CONSTITUTIONAL DIAGRAM

The major features of the uranium-lead system are agreed upon by all investigators. The diagram shown is from Teitel [1]. The results of Maskrey and Frost [2] differ only in that the compound delta (UPb) is shown to melt congruently at 1280 C and no region of immiscibility is shown above 1280 C. The interpretation of Maskrey and Frost [2] is based on thermal analyses, while Teitel [1] depicts the immiscibility gap on the basis of

chemical analyses of liquated alloy samples. Separated layers formed by liquation analyzed 41 to 43 w/o uranium and 97.4 to 98.5 w/o uranium. It is difficult to account for such a large difference in composition unless a region of immiscibility exists.

The compounds UPb and UPb$_3$ are pyrophoric and are therefore difficult to study. The compound UPb is reported to be more pyrophoric than is UPb$_3$ [2].

The solubility of lead in uranium is quite low, and lead additions have little effect on the phase transformations in uranium. The uranium-rich eutectic is reported to occur at 99.6 w/o uranium.[2]

The solubility of uranium in lead has been determined by Teitel [5], who quotes solubilities of 0.002, 0.046, 0.26, and 0.59 w/o at 416, 612, 806, and 1000 C, respectively.

CRYSTALLOGRAPHY

The structure of UPb has been reported by Teitel [5]. Numerous determinations of the structure of UPb$_3$ have been made, and parameters of 4.73 A [4], 4.795 A [3], and 4.7934 A [2] have been reported. The structure in the tabulation is from Maskrey and Frost [2], but the parameter is from Teitel [5].

Phase	Unit cell			Density, g/cm^3		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta (UPb)	Bc tetragonal	$a = 11.04$ $c = 10.60$	48	13.7			
Epsilon (UPb$_3$)	Simple cubic	$a = 4.791$	1	12.98		Pm3m	L12, AuCu$_3$ ordered structure isomorphous with UAl$_3$, UGa$_3$, UIn$_3$, USi$_3$, UGe$_3$, and USn$_3$

References

1. R. J. TEITEL, "The Lead-Uranium System" (AECD-3173), *J. Metals*, **4**, 397–400 (1952).

2. B. R. T. FROST and J. T. MASKREY, "The System Uranium-Lead" (AERE-M/R 1027) *J. Inst. Metals*, **82** (1), 171–80 (1953).

3. J. M. FITZPATRICK and A. R. KAUFMANN, unpublished information (1950).

4. A. IANDELLI and R. FERRO, *Ann. chim.* (Rome), **42**, 598–606 (1952).

5. R. J. TEITEL, "The Uranium-Lead System," *J. Inst. Metals*, **85**, 409–12 (1956–57).

URANIUM-LUTECIUM

Uranium and lutecium exhibit an immiscibility gap in the liquid state. Solubility of lutecium in liquid uranium is reported to increase from 0.2 w/o at 1150 C to 0.4 w/o at 1250 C.[1]

CRYSTALLOGRAPHY

Nothing is known concerning the possibility of compounds in this system.

Reference

1. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.
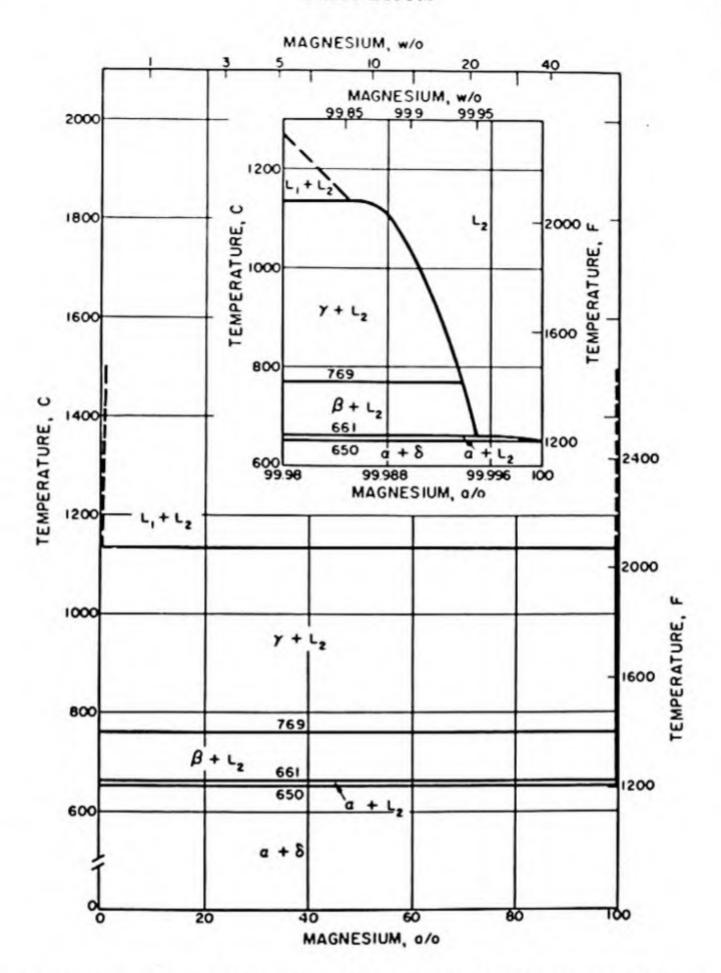
URANIUM-MAGNESIUM

THE CONSTITUTIONAL DIAGRAM

The magnesium-uranium diagram shown has been worked out by investigators at Ames Laboratory.[1] The immiscibility of the two metals has been cited by others [2, 3].

Early work on this system gave evidence of intermetallic phases and thus led to a faulty conception of the system. The later work of Tracy, Chiotti, and Wilhelm [1] provides not only a complete diagram but also an explanation of early erroneous information. It was found that the method of preparation of diffusion and liquation samples was important; if magnesium and uranium were heated together in ordinary crucible materials, uranium carbide or uranium silicide layers, depending on the refractory material, were formed between the uranium and magnesium layers.

Two techniques were found to be especially successful in this work. The first involves heating massive uranium or uranium shavings in molten magnesium in a crucible consisting of 90 w/o magnesium oxide and 10 w/o magnesium fluoride. The other technique consists of melting magnesium and holding it molten in a uranium container. Both methods avoid collection of contaminants at the interface of the two immiscible metals[1].

Diffusion samples prepared by holding magnesium in a uranium crucible for 24 hr at 1015 C showed no evidence of diffusion bands or intermetallic compounds.[1] The work described appears to be quite thorough, since a variety of techniques, including thermal analysis, x-ray studies, microscopic examination and diffusion or liquation tests were utilized.[1]

Uranium and magnesium are almost completely immiscible, even at high temperatures. At 1150 C and 3-atm pressure, 0.14 w/o uranium is soluble in magnesium, while only 0.004 w/o magnesium is soluble in uranium. The solubility of uranium in magnesium is reported to decrease to 0.05 w/o at 675 C and to 0.005 w/o at 650 C.[1] In a more recent determination of uranium solubilities in magnesium, values of 0.002 w/o at 650 C and of 0.17 w/o at 1132 C were obtained.[4]

The melting points of magnesium and uranium and the transformation temperatures in uranium are affected very little in these alloys.
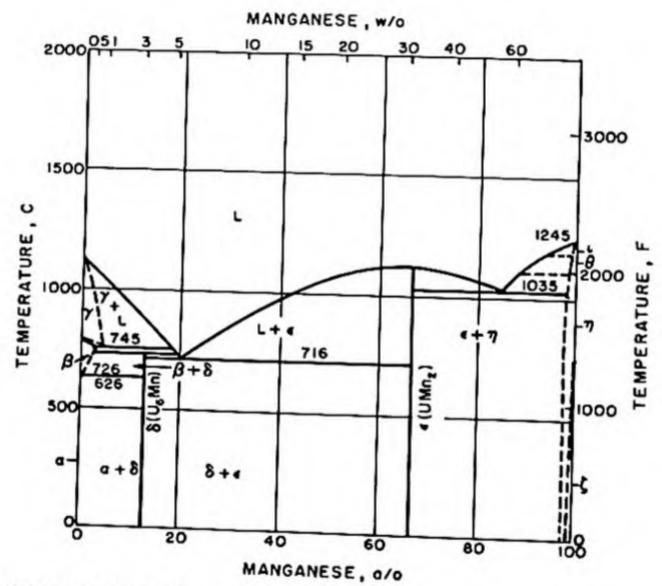
CRYSTALLOGRAPHY

There are no compounds in the uranium-magnesium system.

References

1. P. CHIOTTI, G. A. TRACY and H. A. WILHELM, "Magnesium-Uranium Alloy System," *Trans. AIME*, **206**, 562–67 (1956).

2. AERE, United Kingdom, unpublished information (March, 1947).

3. ALDO IANDELLI and RICARDO FERRO, *Ann. chim.* (Rome), **42**, 598–600 (1952).

4. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704, 2–4 (December, 1957). Classified.

URANIUM-MANGANESE

MANGANESE, w/o

MANGANESE, a/o

THE CONSTITUTIONAL DIAGRAM

The constitutional diagram of uranium-manganese is shown in the accompanying figure [1]. The system has two intermetallic compounds, U_6Mn and UMn_2. The general characteristics of the system are confirmed by data from the United Kingdom.[2] Although some difference in data occurs at the manganese end of the system, there is not enough information available to evaluate this region. Data from the United Kingdom [2] indicate that gamma manganese, designated theta, is stabilized to room temperature by small additions of uranium. On the other hand,

Wilhelm [1] reports that beta manganese, designated as zeta, is stabilized to room temperature in the region between epsilon (UMn_2) and 100 per cent manganese. All data indicate that uranium is soluble in manganese to some extent, but little actual detail is known.

It has been reported [2] and confirmed [3] that beta uranium can be retained by small additions of manganese.

The solubility of manganese in uranium has been reported to be less than 4.3 a/o manganese (1 w/o) in the gamma and about 1.1 a/o manganese at 626 C [1].

CRYSTALLOGRAPHY

The structures of U_6Mn and UMn_2 are described in the tabulation. The intermetallic compound U_6Mn has been thoroughly studied by Baenziger [4] and is isomorphous with U_6Fe, U_6Co, U_6Ni. It has a unit cell volume of about 550 A^3, which is quite close to the volume determined or estimated by addition of atomic volumes. The atomic positions can be described on the basis of space group I4/mcm, although a possible variation from these positions in space groups I42 and I4c2 has not been eliminated.

Nearly identical data have been reported for UMn_2 by Baenziger [4] and by Bowles [5]. The data tabulated are from Baenziger. The compound UMn_2 is the C15-type $MgCu_2$ structure. Bowles reports the lattice constant to be $a = 7.146$ A. The compound UMn_2 is isomorphous with UCo_2 and UFe_2 and may be isomorphous with other uranium compounds. The compound UNi_2, however, is unique and crystallizes in the C14-type $MgZn_2$ structure. Ternary alloys involving these phases are reported in the section devoted to ternary alloys.
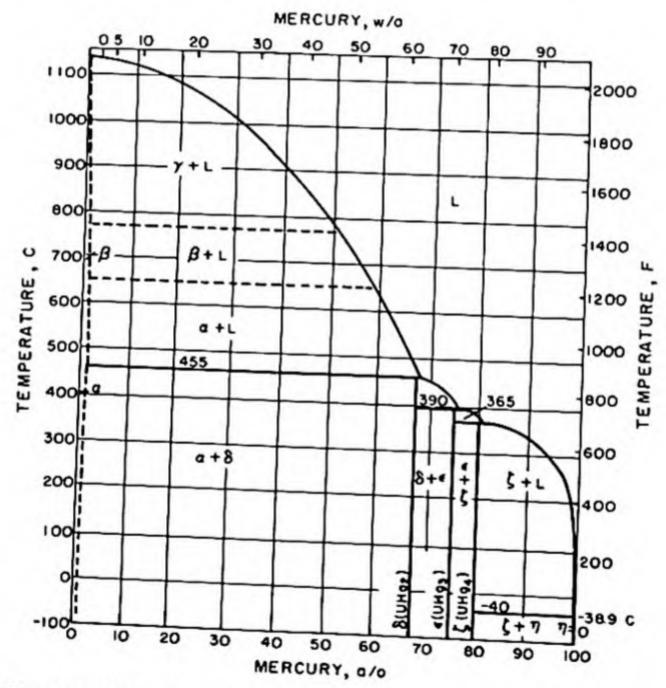
Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta (U_6Mn)	Bc tetragonal	$a = 10.20$ $c = 5.24$	4	17.8		I4/mcm, I42 or I4c2	Isomorphous with U_6Fe, U_6Ni and U_6Co
Epsilon (UMn_2)	Fcc	$a = 7.1484$ ± 0.0014	8	12.57		Fd3m	C15-type, $MgCu_2$ structure; isomorphous with UFe_2 and UCo_2

References

1. H. A. WILHELM and O. N. CARLSON, "The Uranium-Manganese and Uranium-Copper Alloy Systems" (AECD-2717), *Trans. Am. Soc. Metals*, **42**, 1311 (1950).

2. AERE, United Kingdom, unpublished information (May, 1950).

3. H. A. SALLER and F. A. ROUGH, private communication (1949).

4. N. C. BAENZIGER, R. E. RUNDLE, A. I. SNOW and A. S. WILSON, "Compounds of Uranium with Transition Metals of the First Long Period" (AECD-2598), *Acta Cryst.*, **3**, 34–40 (1950).

5. P. I. BOWLES, T. S. HUTCHISON, P. C. L. PFEIL and M. B. WALDRON, "The Crystal Structure of the Compound UMn$_2$ and a Discussion of Laves Phases in Uranium Alloys," AERE-M/R 581 (October, 1950).

URANIUM-MERCURY

THE CONSTITUTIONAL DIAGRAM

The uranium-mercury system has been studied by Wilson [1] and by Frost [2], with virtually identical results. The essential difference was that Frost studied the system by sealing samples and allowing the pressure to rise, while Wilson worked at a pressure of 1 atm. The diagram shown is that of Frost [2]. Since data above the boiling point of mercury (358 C)

were obtained by means of a sealed system, the pressure varied and was as high as several hundred atmospheres.

The diagram of Wilson [1] is identical, except that mercury vapor was in equilibrium with the uranium-mercury compounds and with uranium above the boiling point of mercury.

This is a very difficult system to study. A special means of preparing alloys is necessary, the high vapor pressure of mercury presents a special problem, and the intermetallic compounds are pyrophoric in nature and therefore require special techniques in handling.

It is of interest that Wilson and Frost used the same method of alloy preparation. Essentially, it consists of hydriding uranium, dehydriding under vacuum, and reacting mercury with the resulting uranium powder.

CRYSTALLOGRAPHY

The tabulated data for UHg_2, UHg_3 and UHg_4 are from Rundle [3]. Frost has reported similar information for UHg_2 and UHg_3 but was unable to obtain a more certain analysis of the UHg_4 structure. According to Frost, UHg_2 has a complex hexagonal structure with $a = 4.934$ A and $c = 3.503$ A, while UHg_3 is close-packed hexagonal with $a = 3.320$ A and $c = 4.875$ A. The UHg_3 structure is reported to be a random structure.[1]

It is reported that the unit cell volumes of these compounds, within the limit of accuracy of the work, are equal to the additive atomic volumes. This equivalence is interpreted to mean that the binding is purely metallic in nature.[1]
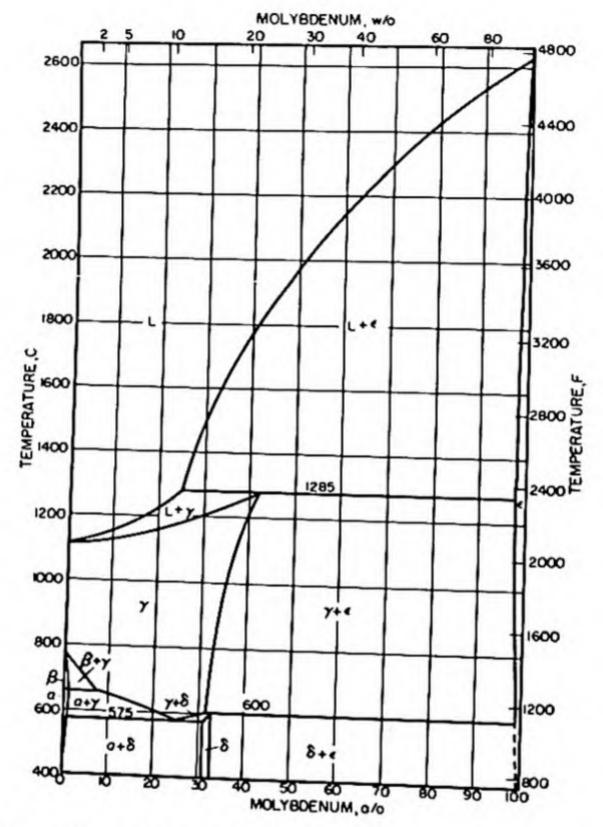
Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta (UHg_2)	Hexagonal	$a = 4.99$ ± 0.01 $c = 3.23$ ± 0.01	1	15.29	15.3	C6/mmm	C32-type, AlB_2 structure
Epsilon (UHg_3)	Hexagonal	$a = 3.327$ ± 0.005 $c = 4.888$ ± 0.005	½	14.88			
Zeta (UHg_4)	Bcc	$a = 3.63$	2	14.5			Tentative analysis

References

1. A. S. WILSON, D. H. AHMANN and R. R. BALDWIN, "The Uranium-Mercury System," CT-2960 (October, 1945).

2. B. R. T. FROST, "The System Uranium-Mercury" (AERE-M/R 1208), J. Inst. Metals, 82 (9), 456–62 (1954).

3. R. E. RUNDLE and A. S. WILSON, "The Structures of Some Metal Compounds" (AECD-2388), Acta Cryst., 2, 148–50 (1949).

URANIUM-MOLYBDENUM

THE CONSTITUTIONAL DIAGRAM

The uranium-molybdenum system was studied first by Ahmann [1], who interpreted the system much as it is now except that the gamma phase was reported to be stabilized to room temperature in the vicinity of 25 to 30 a/o molybdenum. A somewhat similar report was issued in-dependently by Pfeil [2]. It was then shown that the gamma phase is metastable, and, although relatively long periods of time are necessary to transform the gamma, a different phase is stable below about 575 to 600 C [3, 4, 5].

Work by Halteman and Lustman [6] and by Pfeil and Browne [7] has been concentrated on the region of metastable gamma alloys. Early

results indicated that the intermediate delta phase exhibited a wide solubility range from about 20 to 33 a/o molybdenum at the isotherm temperatures. When annealing times on the order of a month are involved, this wide solubility range is observed. However, Halteman [8] has since demonstrated that still more prolonged annealing narrows the region to about 31.5 to 32.5 a/o molybdenum. The diagram shown is based upon these results and confirms the earlier interpretation of Saller, Rough, and Vaughan [3].

There appears to be some difference of opinion regarding the solubility of molybdenum in alpha uranium. Pfeil [2] has reported a peritectoid alpha formation with a solubility of about 3 or 4 a/o molybdenum in alpha. This report is contrary to the work of both Ahmann [1] and Saller [3], who carried out an intensive study of this region. It is true that several a/o of molybdenum can be retained in what might be described as a supersaturated, or distorted, alphalike structure. However, cold working followed by annealing for long periods produces two-phase structures that indicate a maximum solubility of about 0.5 a/o molybdenum, or less, in the alpha. Thermal analyses also indicate a lowering of the beta-to-alpha transformation, even during heating [3]. The maximum solubility in the beta phase is about 1.0 a/o molybdenum. It has been demonstrated that the beta phase can be retained to room temperature by quenching alloys of about 1 a/o molybdenum. The retained structure is metastable and transforms slowly during long periods of room-temperature aging.[3]

The solubility of uranium in molybdenum is quite limited and appears to be a maximum of about 2 a/o uranium at 1285 C [9].

CRYSTALLOGRAPHY

The delta phase has been studied by a number of investigators, and it is generally agreed that it is an ordered structure. The data in the tabulation are from the work of Halteman [8], who reports that the tetragonal delta phase is of the C11b $MoSi_2$ type and can be considered as an ordered form of gamma in which the molybdenum atoms assume special positions in a unit cell composed of three body-centered pseudocubes.

Pfeil and Browne [7] had earlier reported the structure to be body-centered tetragonal with $a = 3.425$ A and $c = 3.282$ A, which is the same structure reported by Tucker [4]. However, the diffraction pattern reported by Tucker was found to be incomplete; also, the observed intensities could not be accounted for on the basis of this structure. Upon this basis, Saller [3] and Halteman [6] had proposed a body-centered tetragonal phase with $a = 6.84$ A and $c = 6.55$ A. However, the more detailed analysis of Halteman [8] leads to the tetragonal cell with $a = 3.427$ A and $c = 9.834$.

| Phase | Unit cell | | | Density, g cm³ | | Space group | Remarks |
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta	Tetrag-onal	$a = 3.427$ $c = 9.834$	2		16.63	I4/mmm	C11b-type isomor-phous with $MoSi_2$, WSi_2, $ReSi_2$, $AlCr_2$, and MgH_2

References

1. D. Ahmann, A. I. Snow and A. S. Wilson, "The Uranium-Molybdenum Binary System," CT-2946 (July, 1945).

2. P. C. L. Pfeil, "The Constitution of Uranium-Molybdenum Alloys," J. Inst. of Metals, 77, 553–70 (1950–51).

3. H. A. Saller, F. A. Rough and D. A. Vaughan, "The Constitution Diagram of Uranium-Rich Uranium-Molybdenum Alloys," BMI-72 (June, 1951).

4. C. W. Tucker, "Discussion on 'The Constitution of Uranium-Molybdenum Alloys' by P. C. L. Pfeil in the J. Inst. of Metals (AECD-3092)," J. Inst. Metals, 78, 760 (1950–51).

5. A. U. Seybolt, "Discussion on 'The Constitution of Uranium-Molybdenum Alloys' by P. C. L. Pfeil in the J. Inst. of Metals (AECD-3093)," J. Inst. Metals, 78, 760 (1950–51).

6. E. K. Halteman and B. Lustman, unpublished information (1954).

7. P. C. L. Pfeil and J. D. Browne, "Superlattice Formation in Uranium-Molybdenum Alloys," AERE M/R 1333 (1954).

8. E. K. Halteman, "The Crystal Structure of U_2Mo," Acta Cryst., 10, 166–69 (March 10, 1957).

9. H. A. Saller, F. A. Rough and D. C. Bennett, "The Constitution of Molybdenum-Rich Uranium-Molybdenum Alloys," BMI-730 (March, 1952).

URANIUM-NEODYMIUM

Neodymium is only partially miscible with uranium in the liquid state.[1, 2] The solubility of neodymium in uranium is reported to increase from 0.15 w/o at 1150 C to 0.2 w/o at 1250 C. Solubility of uranium in neodymium is given as 1.1 w/o at 1000 C and 2.0 w/o at 1250 C.[2]
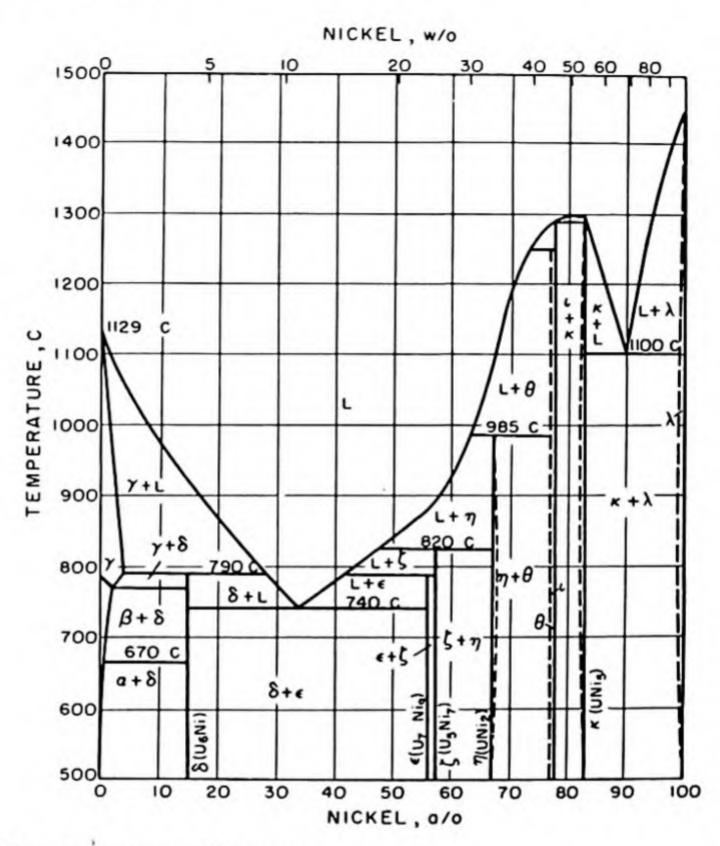
CRYSTALLOGRAPHY

Probably there are no compounds in the uranium-neodymium system.

References

1. National Physical Laboratory, United Kingdom, unpublished information (1949–1950).

2. H. A. Wilhelm, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.

URANIUM-NICKEL

NICKEL, w/o

THE CONSTITUTIONAL DIAGRAM

The diagram shown for the uranium-nickel system is the work of Grogan and Pleasance [1]. Its general shape is similar to that reported by Foote [2], except for the fact that Grogan reports seven intermetallic compounds while Foote reports only four. The structures of U_6Ni, UNi_2, and UNi_5 have been worked out by Baenziger [3]. Attempts by Baenziger to analyze the x-ray pattern presumed to correspond to UNi revealed that the structure was too complex to interpret on the basis of the powder data available. Williams, in an appendix to the report of Grogan [1], has resolved x-ray data of alloys in this region into two separate patterns designated as U_7Ni_9 and U_5Ni_7, although the structures have not been determined.

Intermediate between UNi_2 and UNi_5, another pair of compounds has been proposed by Grogan. Patterns of x-ray diffraction maxima are re-

ported for these materials, although the structures have not been determined [1]. The existence of both compounds was proposed after fairly elaborate heat-treating experiments and examination by a variety of techniques.

Alloys in the range of 40 to 47 w/o nickel were found to have some malleability and could be flattened with a hammer, although cracking occurred in the process. This behavior is reported [1] to be unlike that of the other compounds, which were brittle.

The solubilities in the terminal phases are quite limited.[1, 2] Solubility in the gamma-uranium appears to be a maximum of about 2 a/o nickel at the U_6Ni peritectic temperature. It decreases to about 1.25 a/o at the gamma-to-beta eutectoid. The beta solubility at the gamma-to-beta eutectoid appears to be about 1.0 a/o nickel and decreases sharply to perhaps 0.1 a/o nickel at 700 C. The solubility of nickel in alpha uranium is quite small at all temperatures.

CRYSTALLOGRAPHY

The compound U_6Ni together with the compounds U_6Fe, U_6Co, and U_6Mn have been studied by Baenziger [3]. All have a unit-cell volume nearly equal the volume obtained by addition of atomic values, or about 550 A^3. The atomic positions can be described on the basis of space group I4/mcm, although a possible variation from these positions in space groups I42 and I4c2 has not been eliminated.

Nearly identical data have been reported for UNi_2 by Baenziger [3] and by Bowles [4]. The data in the tabulation are from Baenziger. The UNi_2 structure is the C14-type, $MgZn_2$ structure, unlike UFe_2, UMn_2, and UCo_2, which are the C15-type, $MgCu_2$ structure. Ternary alloys involving these phases are reported in the section devoted to ternary alloys.

The structure of UNi_5 has been studied by Baenziger [3] with the results tabulated below.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta (U_6Ni)	Be tetragonal	$a = 10.37$ ± 0.04 $c = 5.31$ ± 0.02	4	17.6		I4/mcm, I42, or I4c2	Isomorphous with U_6Fe, U_6Co, and U_6Mn
Zeta (UNi_2)	Hexagonal	$a = 4.966$ $c = 8.252$	4	13.46		C6/mmc	C14-type, $MgZn_2$ structure
Kappa (UNi_5)	Fcc	$a = 6.7830$ ± 0.0005	4			F43m or F23	Similar to $MgCu_2$ structure, but of lower symmetry; isomorphous with UCu_5, $PdBe_5$, and $AuBe_5$

References

1. J. D. GROGAN and R. J. PLEASANCE, "A Survey of the Uranium-Nickel System," *J. Inst. Metals.* **82**, 141–47 (1953–54).

2. FRANK FOOTE, J. R. CLARK, M. CIESLICKI, B. J. NELSON and T. R. LANE, "The Tuballoy-Nickel Phase Diagram," CT-3013 (May, 1945).

3. N. C. BAENZIGER, R. E. RUNDLE, A. I. SNOW and A. S. WILSON, "Compounds of Uranium With the Transition Metals of the First Long Period" (AECD-2598), *Acta Cryst.*, **3**, 34–40 (1950).

4. P. J. BOWLES, T. S. HUTCHISON, P. C. L. PFEIL and M. B. WALDRON, "The Crystal Structure of the Compound UMn_2 and a Discussion of Laves Phases in Uranium Alloys," AERE-M/R 581 (October, 1950).
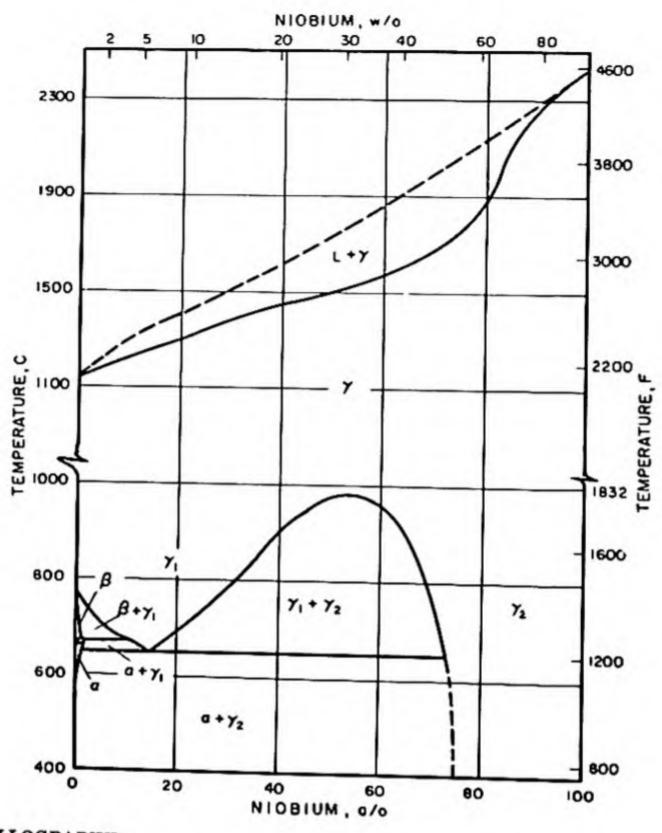
URANIUM-NIOBIUM

THE CONSTITUTIONAL DIAGRAM

The diagram shown is from Rogers [1] and Browne [2], and represents essential confirmation of work of earlier investigators [3, 4], although revisions in certain boundaries have been made.

The complete solubility of gamma uranium and niobium is agreed on by all investigators [1–5], although there is disagreement as to the extent of the gamma$_1$-plus-gamma$_2$ region. Sawyer [3] reports the region as extending from about 11 to 78 a/o at 645 C, while Rogers [1] and Browne [2] report the monotectoid to occur at 16 ± 1 a/o niobium and 645 C, but give values of 73 and 70 a/o, respectively, for the niobium-rich limit of the gamma$_1$-plus-gamma$_2$ region at this temperature. Dwight [5] reports the monotectoid as occurring at 19 a/o niobium and 634 C, the latter temperature being in agreement with its determination by Bauer [6].

On the basis of a tetragonal structure observed in quenched alloys containing 14 to 20 a/o niobium and thermal arrests ranging in temperature from 675 to 725 C for alloys containing 9.6 to 17 a/o niobium, Dwight suggests an ordering of the gamma phase in the region of the monotectoid [5]. While additional investigation is required, the tetragonal structure may be ascribed to a transition structure in the metastable-gamma decomposition.

There is some question concerning the nature of the alpha-to-beta transformation at the uranium-rich end of the system. Although most investigators [2, 3, 5, 6] agree that the reaction occurs peritectoidally, alpha has also been described as forming in a eutectoid reaction [1, 4]. A shift of less than ±5 C in the alpha-to-beta transition temperature is agreed to by all investigators.

Solubilities in the alpha and beta phase are reported to be extremely limited. Browne [2] gives the maximum solubility in each phase as being between 1 and 2 a/o niobium.

CRYSTALLOGRAPHY

There are no compounds in the uranium-niobium system.

References

1. B. A. ROGERS, D. F. ATKINS, E. J. MANTHOS and M. E. KIRKPATRICK, "Uranium-Columbium Alloy Diagram," Paper 7, Nuclear Eng. and Sci. Congress (1957).

2. J. D. BROWNE, P. C. L. PFEIL and G. K. WILLIAMSON, United Kingdom, unpublished information (1957).

3. B. SAWYER, "The Uranium-Columbium Alloy System," ANL-4027 (October, 1946).

4. H. A. SALLER and F. A. ROUGH, private communication (June, 1952).

5. A. E. DWIGHT and M. H. MUELLER, "Constitution of Uranium-Rich Uranium-Niobium and Uranium-Niobium-Zirconium Systems," ANL-5581 (October, 1957).

6. A. A. BAUER, private communication (1957).

URANIUM-NITROGEN

Although no diagram has been constructed for the uranium-nitrogen system, considerable information is available. Katz and Rabinowitch [1] have surveyed the work on the system and report the existence of three compounds, UN, U_2N_3, and UN_2. The system is two phase between the mononitride, UN, and the sesquinitride, U_2N_3. Continuous solubility has been proposed between U_2N_3 and UN_2, since the U_2N_3 lattice is a distorted-fluorite structure, and the UN_2 lattice is a fluorite-type structure.[2] This is questioned by work of Vaughan [3] who reports that U_2N_3 has a hexagonal structure. The structures are discussed in detail in the section on crystallography below.

The mononitride, UN, melts at about 2630 ± 50 C.[4] It is quite stable in vacuum at 1700 C, and sinters at 2300 C.[1]

The sesquinitride, U_2N_3, loses nitrogen in vacuum at temperatures above 700 to 800 C. It is stable only to 1300 C, where it decomposes to form UN plus N_2 at low pressures.[1] Under high pressures, U_2N_3 decomposes to UN plus UN_2 at about 1300 C, with a volume decrease of about 13 per cent.[2]

The solubility of nitrogen in uranium is limited. The solubility of uranium in the mononitride, UN, is also limited.[1]

Early reports of U_4N_7 seem to be attributable to the observation that the U-plus-N_2 reaction at 1-atm pressure reaches a maximum composition of $UN_{1.75}$.[2]

CRYSTALLOGRAPHY

The tabulated lattice constants and data for UN, U_2N_3, and UN_2 are from the work of Rundle [2]. The lattice constant of UN has varied as much as 4.899 A. This extreme variation is attributed to the presence of carbon or oxygen instead of solubility of nitrogen in UN. It is very difficult to avoid small amounts of these contaminants during preparation.[2]

As the nitrogen-to-oxygen ratio is increased from 1.5 to 1.75, the U_2N_3 lattice constant decreases from 10.678 to 10.580 A; from 1.75 to 2.00 it in-

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
UN	Fcc	$a = 4.880$ ± 0.001	4	14.32			NaCl structure, completely soluble with UC
U_2N_3	Bcc	$a = 10.678$ ± 0.005	16	11.24		Ia3	Distorted-fluorite structure, isomorphous with Mn_2O_3
UN_2	Pseudo-fcc	$a = 5.31$		11.73			Fluorite structure

creases from 10.580 to 10.62 (2 × 5.31) Å. The decrease is interpreted to mean that there is solubility over the entire range between the distorted-fluorite structure of U_2N_3 and the fluorite structure of UN_2.[2]

Vaughan [3], on the other hand, reports that U_2N_3 has a hexagonal lattice with $a = 3.70$ and $c = 5.80$ Å. This structure appears to be consistent with the structure of Th_2N_3, which is hexagonal with $a = 3.87$ and $c = 6.16$ Å.

References

1. J. J. Katz and E. Rabinowitch, *The Chemistry of Uranium, Part I*, McGraw-Hill Book Company, Inc., New York (1951), 232–41.

2. R. E. Rundle, N. C. Baenziger, A. S. Wilson and R. A. McDonald, "The Structures of the Carbides, Nitrides and Oxides of Uranium," *J. Am. Chem. Soc.*, **70**, 99–105 (1948).

3. D. A. Vaughan and C. M. Schwartz, unpublished information (April, 1954).

4. Premo Chiotti, "Experimental Refractory Bodies of High-Melting Nitrides, Carbides and Uranium Dioxide," *J. Am. Ceram. Soc.*, **35**, 123–30 (May, 1952).

5. Leo Brewer, L. Bromley, P. W. Gilles and N. L. Lofgren, "The Thermodynamic Properties and Equilibrium at High Temperatures of Uranium Halides, Oxides, Nitrides and Carbides," MDDC-1543, 85 (September, 1945).

URANIUM-OSMIUM

A partial diagram has been constructed by Park [1], although features in the system are tentative.

Apparently, a minimum of two compounds exists in the system. The first uranium-rich compound decomposes peritectically at a temperature below that of the eutectic temperature.[1] A second compound has been identified as UOs_2.[2] Osmium is reported to stabilize the gamma and beta phases.[1]
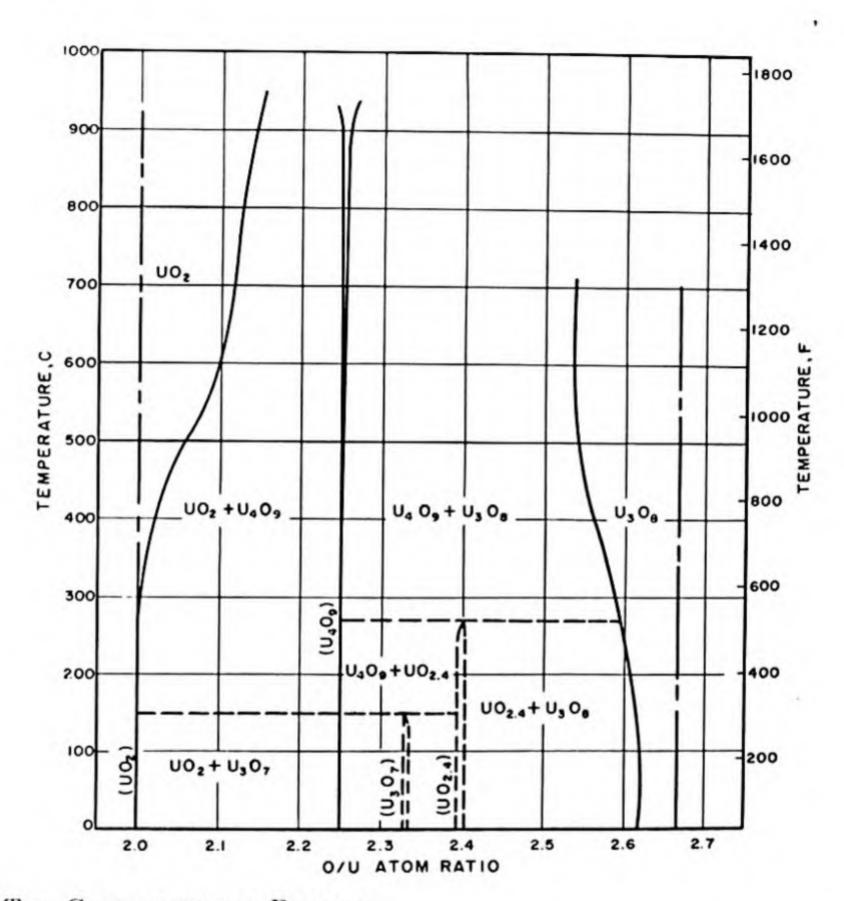
CRYSTALLOGRAPHY

Data are available for only one compound UOs_2.[2]

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, Å	Number of molecules	X-ray	Other		
UOs_2	Fcc	7.5125 ± 0.0005	8	19.42		Fd3m	C15, $MgCu_2$ structure

References

1. J. J. Park, private communication (October, 1956).

2. T. J. Heal and G. I. Williams, "Compounds of Uranium With Transition Metals of the Second and Third Long Periods," *Acta Cryst.*, **8**, 494 (1955).

URANIUM-OXYGEN

THE CONSTITUTIONAL DIAGRAM

Although much work has been done on the system, the constitution of uranium-oxygen alloys is somewhat uncertain. Katz and Rabinowitch [1] reviewed the system in considerable detail, but were unable to resolve all of the areas of conflicting information. Apparently, experimental results and interpretation are highly dependent upon the starting materials and method of specimen preparation.

The solubility of oxygen in uranium is small even in the liquid state. Cleaves [2] observed solubilities of about 0.05 a/o oxygen at the melting point of uranium and about 0.1 a/o and 0.4 a/o oxygen at 1400 and 2000 C, respectively.

The solubility in solid uranium is even less; it is difficult to determine exactly because of the presence of other minor impurities [3].

The region between UO_2 and U_3O_8 has been studied more intensively than any other portion of the system. The diagram shown for this region is from Gronvold [4] and is similar to the diagram published by Perio [5] with the major refinement being that Gronvold shows a solid solution range of oxygen in UO_2 at elevated temperatures. Vaughan and Schwartz [6] and Willardson [7] report a wider solubility range both at room and elevated temperatures; at room temperature the range is reported as UO_2 to about $UO_{2.10}$.

There appears to be fairly general agreement on the existence of three stable uranium oxides in the range shown: (1) the fluorite-type dioxide (UO_2); (2) the oxide U_4O_9 (also reported as beta UO_2), which maintains the fluorite structure with the apparent addition of an interstitial oxygen atom; and (3) the orthorhombic oxide (U_3O_8).

One or more tetragonal oxides form in the region from $UO_{2.30}$ to $UO_{2.40}$. However, the stability of these phases appears to be questionable. The phase relationships shown with respect to these oxides are based upon the examination of specimens prepared by the low-temperature oxidation of UO_2 as reported by Gronvold and Haraldsen [8]. Perio [5] and Vaughan and Schwartz [6] report similar results when essentially the same techniques are employed. Although Hering and Perio [9] have reported the reversible formation of $UO_{2.40}$ from UO_2 and U_3O_8, when specimens are homogenized at elevated temperatures the tetragonal oxides apparently do not form on succeeding prolonged low-temperature anneals [4, 5, 6, 10]. On this basis it appears that the phase relationships shown by the dotted lines, which were drawn by Gronvold to indicate the temperature at which transformation takes place at an appreciable rate, may represent metastable nonequilibrium conditions. At any rate, there is agreement that the tetragonal oxides decompose to U_4O_9 and U_3O_8 on heating at elevated temperatures. However, there is some variation in the temperature reported for this decomposition. Alberman and Anderson [10] report the decomposition as occurring above 230 C, Gronvold and Haraldsen [8] above 270 C, and Perio [9] at 480 to 500 C. Vaughan and Schwartz [6] and Willardson [7] are in general agreement with Perio on this point.

Since the tetragonal phase exists over a limited temperature range, there is no conflict with data of Biltz and Muller [11], who determined by tensiometric studies that a two-phase region exists at 1200 C between $UO_{2.31}$ and $UO_{2.61}$. Hoekstra and Siegel [12] have confirmed these phase limits and give $UO_{2.60}$ as the lower limit of U_3O_8. Baenziger [13] and Rundle [14] on the other hand report the existence of U_2O_5 (composition $UO_{2.50}$), which seems to be generally interpreted as being the same structure as U_3O_8 [1, 9, 10, 12].

The upper limit of U_3O_8 is in question. Hering and Perio [9] report a definite limit at 2.67. On the other hand, Katz and Rabinowitch [1] report that the similarity of the U_3O_8 and one of the UO_3 structures makes a gradual and continuous transition between the two both possible and plausible.

In addition to the oxides shown in the region from UO_2 to U_3O_8, the sodium chloride-type monoxide (UO) and the trioxide (UO_3) with three allotropic modifications [1] have seen reported.

The melting point of UO_2 is about 2875 C [15].

CRYSTALLOGRAPHY

The monoxide (UO) has the sodium chloride-type structure. There appears to be limited solubility of oxygen in UO, and the lattice constant does not vary greatly. The tabulated data for UO are from the works of Rundle [14]. However, there is some question about the stability of the UO phase. UO, UN, and UC are reported to be isomorphous [12], and on the basis of the inability [6] to prepare an extremely pure sample of UO, this phase may represent a solution of oxygen in the nitride or carbide lattice.

Uranium dioxide is cubic and has the fluorite-type structure. The data for UO_2 are also from Rundle. Numerous data on UO_2 are summarized by Katz and Rabinowitch [1] that show a variety of values for the UO_2 lattice constant. These generally fall within the lattice constants given by Rundle, who reports that the UO_2 lattice can be increased to $a = 5.4720 \pm 0.0007$ A by heating UO_2 with uranium. Similarly, it can be decreased to $a = 5.4407 \pm 0.0008$ A by increasing the oxygen content.

The data for the U_4O_9 phase are from Gronvold [4]. The high density, 11.159 g/cm^3, is taken as evidence of the interstitial solubility of oxygen in the fluorite UO_2-like structure.

It is difficult to determine whether a single phase with a wide solubility range or whether more than one tetragonal phase exists in the region $UO_{2.30}$ to $UO_{2.40}$. Diffusion is very slow at the temperatures at which these phases form, and it is questionable whether equilibrium is attained. The tabulated data for the U_3O_7 phase are from Perio [5]. The tetragonal oxides are apparently characterized by an increase in the c/a ratio with increasing oxygen content.

The oxide U_2O_5 [13, 14] is reported to have an orthorhombic structure with $a = 6.73 \pm 0.02$ A, $b = 31.71 \pm 0.1$ A, and $c = 8.29 \pm 0.02$ A. This structure contains a pseudo cell with $a = 6.73$ A, $b = 3.964$ A, and $c = 4.145$ A, which is closely related to the structure of U_3O_8 (tabulated) as reported by Zachariasen. The pseudo cell is identical with the U_3O_8 structure as reported by Gronvold [8]. For that matter, Rundle reports a

single-phase region between U_2O_5 and U_3O_8 [14]. It appears that the varying reports all concern a continuous series of solid solutions.

X-ray data for two of the three trioxide (UO_3) modifications reported [1] are tabulated. "Alpha" UO_3, tabulated as hexagonal, was reported by Zachariasen [16], and is orange. It was formed by reacting amorphous UO_3 at 500 C for 8 hr under 20 atm of oxygen pressure. The "beta" UO_3, tabulated as orthorhombic, was reported by Perio [17]. It is yellow and was formed by heating amorphous UO_3 in sealed tubes at about 600 to 620 C. Under these same test conditions, UO_3 decomposed at 610 to 740 C to form the orthorhombic U_3O_8 [17].

Additional references are included [18–21].

No anhydrous higher oxides appear to be stable.[1]

| Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, Å	Number of molecules	X-ray	Other		
UO	Fcc	$a = 4.92$	4	13.63			NaCl structure isomorphous with UO and UN
UO_2	Cubic	$a = 5.4691 \pm 0.0005$	4	10.96			Fluorite-type structure isomorphous with ThO_2
U_4O_9	Cubic	$a = 5.4411$			11.159		
U_3O_7	Tetragonal	$a = 5.447 \pm 0.003$ $c = 5.400 \pm 0.002$					
U_3O_8	Orthorhombic	$a = 6.71 \pm 0.01$ $b = 11.96 \pm 0.03$ $c = 4.15 \pm 0.01$	2			Amm	
"Alpha" UO_3	Hexagonal	$a = 3.971 \pm 0.004$ $c = 4.168 \pm 0.008$	1	8.39	8.34	C3̄m	Similar to orthorhombic U_3O_8
"Beta" UO_3	Orthorhombic	$a = 13.01$ $b = 10.72$ $c = 7.51$	16		7.15		
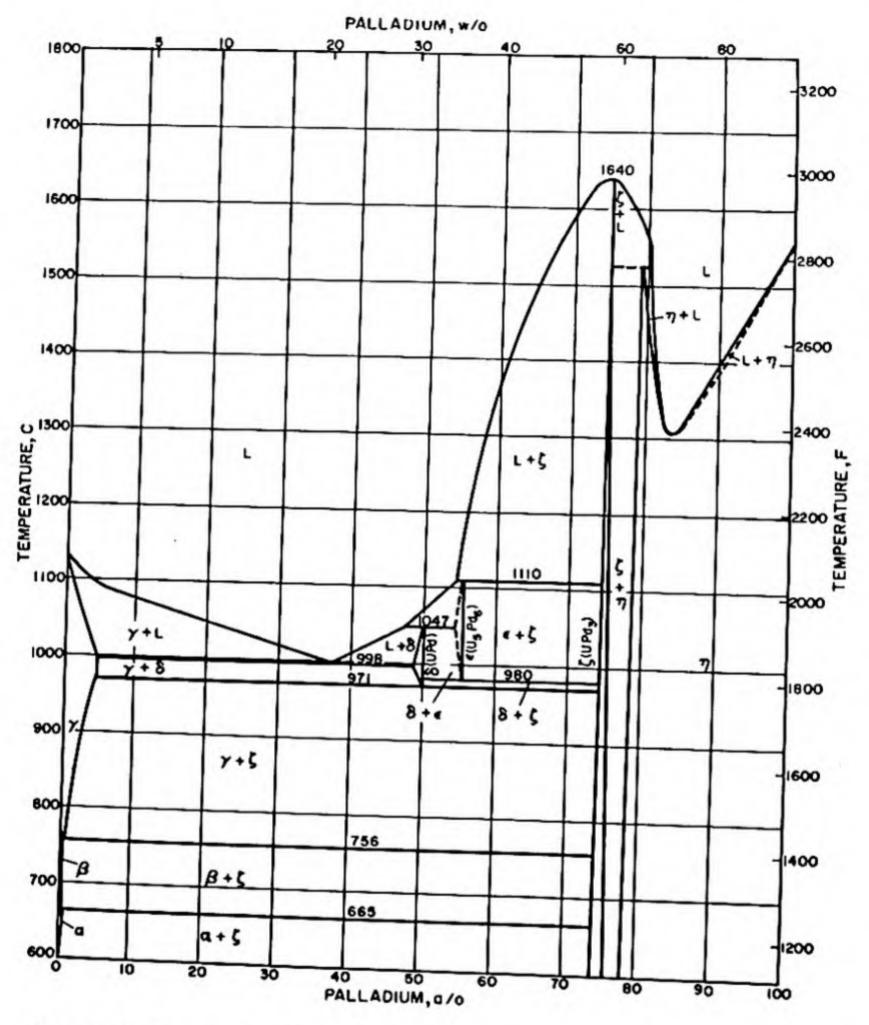
References

1. J. J. KATZ and E. RABINOWITCH, *The Chemistry of Uranium, Part I*, McGraw-Hill Book Company, Inc., New York (1951), pp 224–81.
2. H. E. CLEAVES, M. M. CRON and J. T. STERLING, unpublished information (February, 1954).
3. B. BLUMENTHAL, unpublished information (1952).
4. F. GRONVOLD, *J. Inorg. and Nuclear Chem.*, 1, 357 (1955).

5. P. Perio. "Low Temperature Oxidation of UO_2," *Bull. soc. chim.* (France), pp. 256–63 (1953).

6. D. A. Vaughan, J. R. Bridge and C. M. Schwartz, "Comparison of Active and Inactive Uranium Dioxide-Oxygen Systems," BMI-1241 (December 10, 1957).

7. R. K. Willardson, J. W. Moody and H. L. Goering, "The Electrical Properties of Uranium Oxides," BMI-1135 (September 25, 1956).

8. F. Gronvold and H. Haraldsen, "Crystal Structure of Uranium Oxide (U_3O_8)," *Nature*, 162, 69–70 (1948).

9. H. Hering and P. Perio, "Equilibria of Uranium Oxides Between UO_2 and U_3O_8." *Bull. soc. chim.* (France), pp 351–57 (March–April, 1952).

10. K. B. Alberman and J. S. Anderson, "The Oxides of Uranium," *J. Am. Chem. Soc.*, 2 (Supplementary Issue), S 303–11 (1949).

11. W. Biltz and H. Muller, *Z. anorg. u. allgem. chem.*, 163, 161–295 (1927).

12. H. Hoekstra and S. Siegel, unpublished information (September, 1952).

13. N. C. Baenziger, The Crystal Structure of Some Thorium and Uranium Compounds," AECO-3237 (1948).

14. R. E. Rundle, N. C. Baenziger, A. S. Wilson and R. A. McDonald, "The Structures of the Carbides, Nitrides, and Oxides of Uranium" (MDDC-1608), *J. Am. Chem. Soc.*, 70, 99–105 (1948).

15. L. Brewer, L. Bromley, P. W. Gilles and N. L. Lofgren, "The Thermodynamic Properties and Equilibrium at High Temperatures of Uranium Hydrides, Oxides, Nitrides, and Carbides," MDDC-1543, 85 (September 20, 1945.)

16. W. H. Zachariasen, "Crystal Chemical Studies of the 5 F-Series of Elements," *Acta Cryst.*, 1, 265 (1948).

17. P. Perio, "Crystalline Varieties of UO_3," *Bull. soc. chim.* (France), 776–77 (July–August, 1953).

18. H. R. Hoekstra and J. J. Katz, "Studies on the Uranium-Oxygen System," AECD-2954, 15 (August 10, 1950).

19. E. Slowinski and N. Elliot, "Lattice Constants and Magnetic Susceptibilities of Solid Solutions of Uranium and Thorium Dioxides," *Acta Cryst.*, 5, 768–70 (1952).

20. W. A. Lambertson, M. H. Mueller and F. H. Gunzel, Jr., "Uranium Oxide Phase Equilibrium Systems," *J. Am. Ceram. Soc.*, 36, 329–34, 398-99 (1953).

21. P. Perio, "Observation on Uranium Oxides Formed Between UO_2 and U_3O_8," *Bull. soc. chim.* (France), 840–41 (1953).

URANIUM-PALLADIUM

The Constitutional Diagram

The diagram shown is that of Catterall, Grogan, and Pleasance [1]; it differs in many respects from the tentative diagram of Park [2]. The latter reported two compounds, UPd_2 and U_3Pd_7, stable to room temperature in addition to the congruently melting UPd_3.

The solubility of palladium in uranium is small, being less than 0.3 a/o in both the alpha and beta phases.[1] Solubility in the gamma phase is greater, rising from less than 1.1 a/o at 760 C to 5 a/o at 998 C according to Catterall [1]. These values are in good agreement with those reported by Park [2] of about 4 a/o at 995 C.

The temperature of the peritectoid by which the palladium solid solution forms has not been located exactly, although it exceeds 1425 C and is tentatively estimated to occur at 1525 C. Uranium has a large solubility

in palladium; Catterall [1] quotes solubilities of 22.2 a/o at 700, 800, and 900 C; 21.9 a/o at 1180 C, and 21.8 a/o at 1400 C.

CRYSTALLOGRAPHY

The structure of UPd_3 has been reported by Heal and Williams [3] and confirmed by Catterall [1], who also reported a variation in the lattice parameters with composition; thus, a uranium-rich sample gave $c = 9.641$ A, $a = 5.769$ A, and $c/a = 1.671$, whereas a palladium-rich sample gave $c = 9.526$ A, $a = 5.763$ A. and $c/a = 1.653$.

| Phase | Unit cell | | | Density, g/cm³ | | Space group | Remarks |
	Type	Dimensions, A	Number of molecules	X-ray	Other		
UPd_3	Hexago-nal	$a = 5.769$ $c = 9.640$	4	13.39		P63/mmc	DO 24, $TiNi_3$ structure

References

1. J. A. CATTERALL, J. D. GROGAN and R. J. PLEASANCE, "The System Uranium-Palladium," *J. Inst. Met.*, **85**, 63 (1956–1957).

2. J. J. PARK, private communication (October, 1956).

3. T. J. HEAL and G. I. WILLIAMS, "Compounds of Uranium With the Transition Metals of the Second and Third Long Periods," *Acta Cryst.*, **8**, 494 (1955).

URANIUM-PHOSPHORUS

Several uranium-phosphorus compounds have been reported. No other information is available.
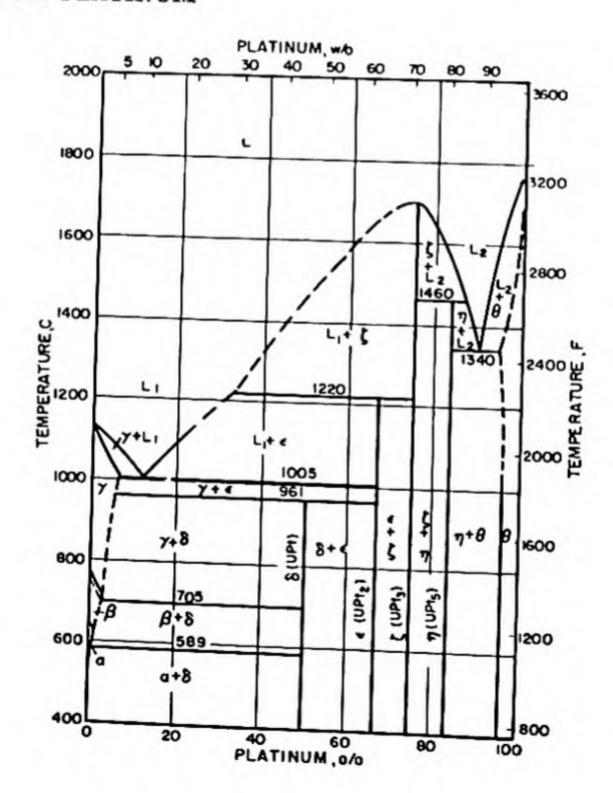
CRYSTALLOGRAPHY

The reported structures of UP [1, 2], U_3P_4 [2], and UP_2 [3] are tabulated below. Additional references are given.[4, 5]

| Phase | Unit cell | | | Remarks |
	Type	Dimensions, A	Number of molecules	
UP	Fcc	$a = 5.589$	4	NaCl-type structure
U_3P_4	Bcc	$a = 8.197$	4	Analogous to Th_3P_4
UP_2	Tetragonal	$a = 3.800$ $c = 7.762$		Isomorphous with UAs_2

References

1. R. E. RUNDLE and N. C. BAENZIGER, unpublished information (1944).

2. M. ZUMBUSCH, "Structural Analogy of Uranium and Thorium Phosphides," *Z. anorg. u. allgem. Chem.*, **245**, 402–8 (1941).

3. A. IANDELLI, "Uranium Arsenides, II: Crystal Structure of UAs$_2$ and UP$_2$," *Atti accad. nazl. Lincei, Rend., Classe sci. fis., mat. e nat.*, **13**, 144–51 (1952).

4. M. HEINBRECHT, M. ZUMBUSCH and W. BILTZ, "Systematic Study of Affinity, XCV: Uranium Phosphides," *Z. anorg. u. allgem. Chem.*, **245**, 391–401 (1941).

5. J. J. KATZ and E. RABINOWITCH, *The Chemistry of Uranium, Part I*, McGraw-Hill Book Company, Inc., New York (1951), 241.

URANIUM-PLATINUM

THE CONSTITUTIONAL DIAGRAM

The system has been studied by Park [1], and a tentative diagram constructed.

Two eutectics occur in the system, one at 12 a/o platinum and another at 90 a/o platinum. Four intermetallic compounds have been identified.

Maximum solubility on the gamma-uranium phase is reported to be 6.5 a/o platinum at the eutectic temperature.[1] Solubilities of about 3.0 and 0.3 a/o in the beta- and alpha-uranium phases, respectively, are indicated.

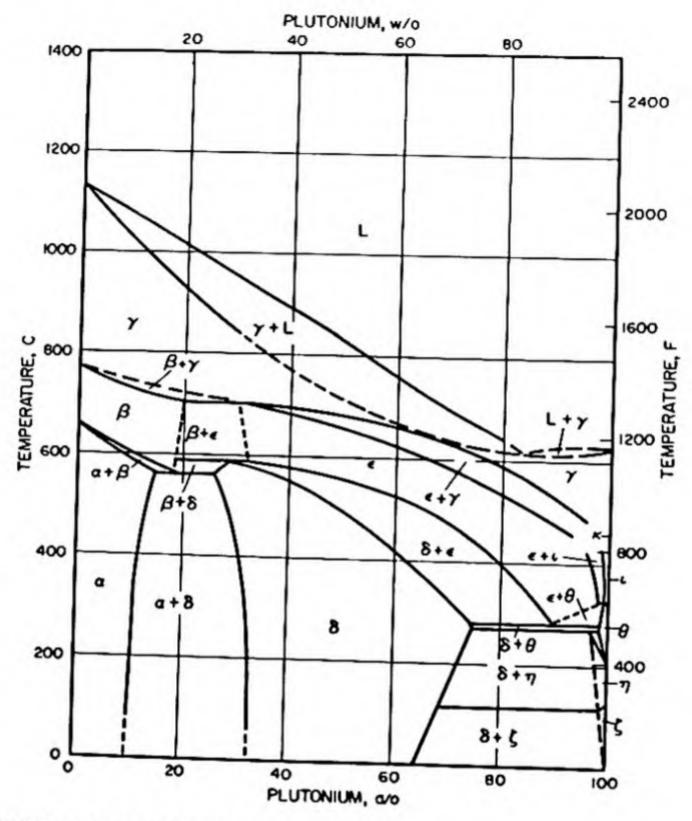Approximately 5 a/o uranium is soluble in platinum.

CRYSTALLOGRAPHY

The crystal structures of UPt_2 [2] and UPt_3 [3] have been determined.

| Phase | Unit cell | | | Density, g/cm³ | | Space group | Remarks |
	Type	Dimensions, Å	Number of molecules	X-ray	Other		
Zeta (UPt_3)	Hexag-onal	$a = 5.764$ $c = 4.898$	2	19.40		$P6_3/mmc$	DO 19, Mg_3Cd structure
Epsilon (UPt_2)	Ortho-rhombic	$a = 4.12$ $b = 9.69$ $c = 5.64$	4	18.54		Cmcm	

References

1. J. J. PARK, private communication (October, 1956).

2. Fulmer Research Institute, United Kingdom, unpublished information (June, 1957).

3. T. J. HEAL and G. I. WILLIAMS, "Compounds of Uranium With the Transition Metals of the Second and Third Long Periods," *Acta Cryst.*, **8**, 494 (1955).

URANIUM-PLUTONIUM

The Constitutional Diagram

Phase relationships in this system are quite complex but have been well defined.[1] The liquidus in the system exhibits a minimum as shown and at elevated temperatures the body-centered cubic forms of uranium and plutonium show complete mutual solubility. Two intermediate phases with extensive ranges of homogeneity are reported. The delta phase extends from 26 to 75 a/o plutonium; the epsilon phase extends from 30 to 98 a/o plutonium.

Crystallography

Tentative structure identification is given below.[1] Because the epsilon phase is not stable at room temperature, difficulty was found in obtaining

good diffraction patterns. The delta phase, while cubic at room temperature, expands anisotropically when heated. The powder pattern splits in accordance with tetragonal symmetry; consequently, the structure given below is for room temperature.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, Å	Number of molecules	X-ray	Other		
Delta	Simple tetrag- onal	$a = 10.57 \pm 0.05$ $c = 10.76 \pm 0.05$	52	17.15			Data for UPu₃ composition
Epsilon	Simple cubic	$a = 10.664$	58	18.95			Data for UPu composition

Reference

1. F. W. SCHONFELD, "Phase Diagram Studies at Los Alamos," ASM Seminar (1957).

URANIUM-PRASEODYMIUM

Uranium and praseodymium are only partially miscible in the liquid state [1, 2]. The solubility of praseodymium in uranium is reported as 0.2 w/o at 1150 C and 0.4 w/o at 1250 C, while the solubility of uranium in praseodymium is given as 1.0 w/o at 1000 C and 2.2 w/o at 1250 C.[2]

CRYSTALLOGRAPHY

Probably there are no compounds in the uranium-praseodymium system.

References

1. National Physical Laboratory, United Kingdom, unpublished information (1949–1950).
2. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.

URANIUM-RHENIUM

While a diagram is not available for the system, a number of observations concerning uranium-rhenium alloys have been reported.[1]

There are apparently two compounds in the system: URe_2 which melts at a temperature in excess of 1200 C, and an ordered structure with a limited temperature range of stability containing 8 to 10 a/o rhenium. At 1000 C

URe_2 exists in equilibrium with gamma uranium which is replaced at 800 C by an optically anisotropic phase with an ordered structure similar to that of U_2Mo. At lower temperatures, beta uranium containing 4 a/o rhenium was found to decompose eutectoidally at 625 to 630 to alpha uranium and URe_2.

Fairly extensive solid solubility of rhenium in gamma uranium is indicated, up to 16 a/o rhenium being retained in solid solution in rapidly cooled small melts. Peritectic formation of the gamma phase is probable, a thermal arrest being detected in a 7.5 a/o rhenium alloy at a temperature of 1150 to 1200 C. The solid-solution region decreases rapidly initially, with about 6 a/o rhenium being soluble in gamma uranium between 800 and 1000 C; little variation in solubility with temperature is observed in this range. The solubility of rhenium in alpha uranium is about 1 a/o at 650 C and decreases to less than 0.5 a/o at 600 C.

The gamma phase can be retained in alloys containing 5 a/o rhenium but decomposition to a distorted alpha structure proceeds at room temperature. The distorted alpha structure is developed on quenching alloys containing 4 a/o rhenium.

CRYSTALLOGRAPHY

The compound URe_2 exhibits two allotropic forms. Above 180 ± 3 C, it has a hexagonal C14-type structure, and below this temperature an orthorhombic structure based on a distorted C14-type structure. The data below are from Hatt [2].
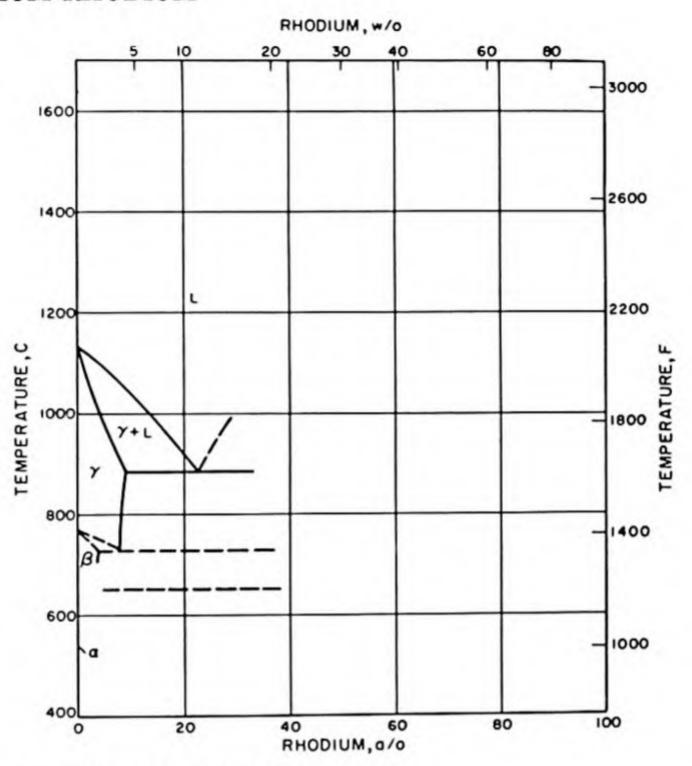
The second compound found in alloys containing about 10 a/o rhenium when quenched from 800 C appears to be similar in structure to U_2Mo of the uranium-molybdenum system. A tentative room-temperature analysis indicates a tetragonal structure with $c/a = 0.98$.[1]

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
URe_2	Ortho-rhombic	$a = 5.600$ $b = 9.178$ $c = 8.463$	8	18.65		Cmcm	Dimensions for 20 C
URe_2	Hexag-onal	$a = 5.433$ $c = 8.561$	4	18.56		$P6_3/mmc$	C14-type; dimensions for 213 C

References

1. Fulmer Research Institute, United Kingdom, unpublished information (June, 1957).

2. B. A. HATT, "The Crystal Structure of URe_2," Fulmer Research Institute Report, R. 53/19 (1955).

URANIUM-RHODIUM

THE CONSTITUTIONAL DIAGRAM

The features shown have been determined by Yorke [1] and are confirmed in form by the work of Park [2]. The eutectic occurs at 22.5 a/o rhodium and 885 C. There is considerable solubility of rhodium in the gamma-uranium phase. Yorke reports solubilities of 9 ± 1 a/o at 885 C and 8.5 ± 1 a/o at 850 C. Park reports the gamma-to-beta transformation is depressed to 730 C.
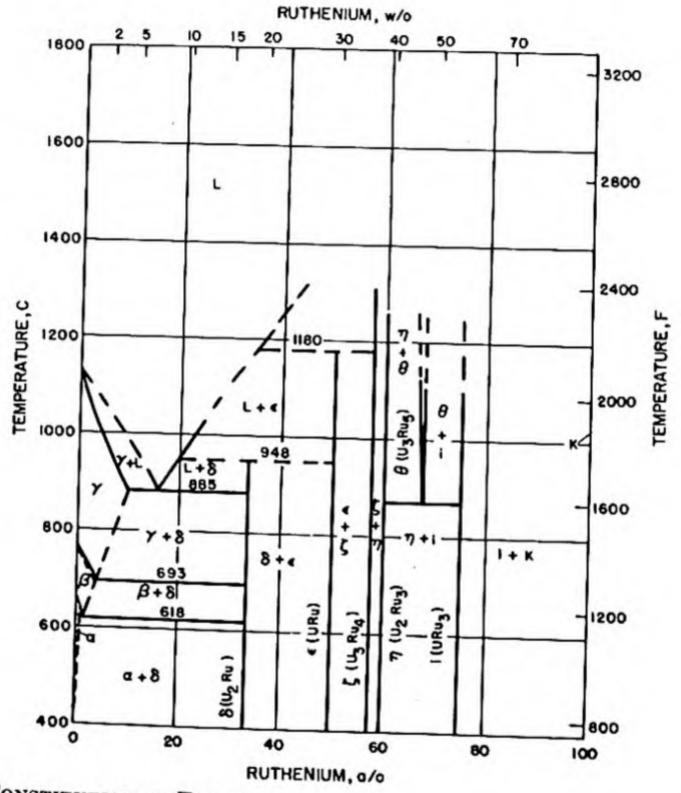
CRYSTALLOGRAPHY

The crystal structure of URh_3 has been determined [3] as below.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
URh_3	Cubic	$a = 3.991$	1			Pm3m	L12-Cu₃Au structure

References

1. J. M. YORKE, "Alloys of Uranium With Ruthenium and Rhodium," Johnson and Matthey Ltd., AERE X/PR 2409 (1956).
2. J. J. PARK, private communication (October, 1956).
3. A. E. DWIGHT, private communication (October 28, 1957).

URANIUM-RUTHENIUM

THE CONSTITUTIONAL DIAGRAM

The diagram shown is based on the work of Park [1] revised to include the data of Dwight [2] in the regions of higher ruthenium content. The features of the high-uranium end of the diagram have also been reported by Murray and Lloyd [3] and by Yorke [4], giving excellent agreement with the work of Park.

Park [1] has investigated only the region up to URu_3 and reports two compounds of lower ruthenium content, U_2Ru and URu. Dwight [2]

reports three additional compounds in this range, between URu and URu_3; these are U_3Ru_4, U_2Ru_3, and U_3Ru_5, the latter decomposing eutectoidally at 870 C to U_2Ru_3 and URu_3.

The addition of ruthenium to uranium lowers the beta-to-gamma and alpha-to-beta transformation temperatures. Park [1] reports values of 693 and 618 C, respectively, for these temperatures and 885 C for the eutectic temperature, while Dwight [2] reports values of 708, 640, and 898 C, respectively.

CRYSTALLOGRAPHY

The crystal structure of URu_3 has been reported by Heal and Williams [5].

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
URu₃	Simple cubic	3.988 ± 0.002	1	14.24		Pm3m	L12-Cu₃Au structure

References

1. J. J. PARK, private communication (October, 1956).

2. A. E. DWIGHT, "Nuclear Fuels Newsletter," WASH-702 (May, 1957); WASH-704 (December, 1957). Classified.

3. J. R. MURRAY and S. J. LLOYD, "Some Observations on Uranium-Rich Uranium-Ruthenium Alloys," AERE M/M 107.

4. J. M. YORKE, "Alloys of Uranium With Ruthenium and Rhodium," AERE X/PR 2409 (1956).

5. T. J. HEAL and G. I. WILLIAMS, "Compounds of Uranium With the Transitions Metals," *Acta Cryst.*, **8**, 494 (1955).

URANIUM-SAMARIUM

Uranium and samarium show little miscibility in the liquid state. The solubility of samarium in liquid uranium is reported to be 0.2 w/o at 1150 C and 0.25 w/o at 1250 C, while uranium solubility in samarium is given as 0.5 w/o at 1000 C and 1.3 w/o at 1250 C.

CRYSTALLOGRAPHY

Data concerning the possibility of compounds in this system are not available.

Reference

1. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.

URANIUM-SELENIUM

Data on the uranium-selenium system are incomplete. Ferro reports the presence of three compounds, USe, U_2Se_3, USe_2, in addition to a selenium-rich phase. The USe_2 may exist in two polymorphic forms. In an earlier review by Katz and Rabinowitch, the compounds U_2Se_3 and USe_2 had been reported.[2]

CRYSTALLOGRAPHY

The crystal structure of USe has been determined by Ferro as given below. A ternary compound, UOSe, occurring in contaminated alloys, has been identified as having tetragonal symmetry and being of the PbFCl-type with $a = 3.901$ A, $c/a = 1.789$.

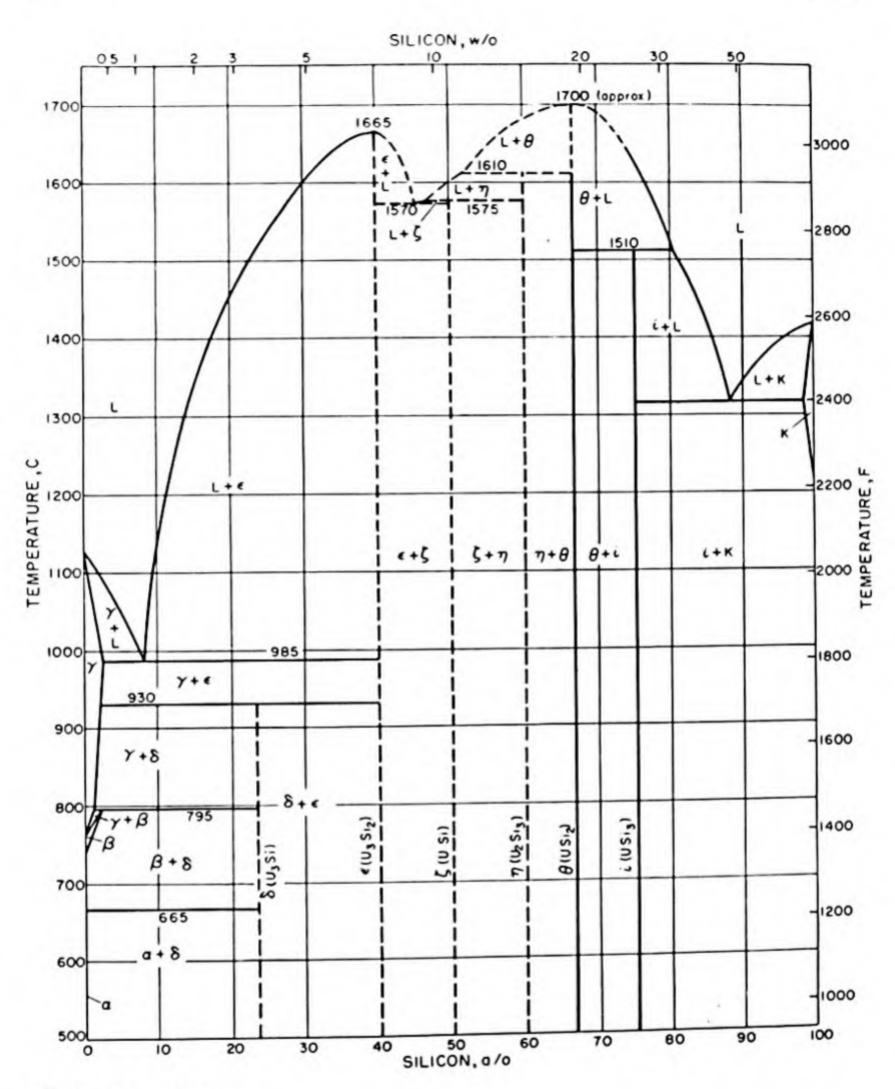| Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
USe	Cubic	$a = 5.750$	4	11.07			NaCl-type structure

References

1. R. FERRO, "Certain Uranium-Selenium and Uranium-Tellurium Compounds," *Z. anorg. u. allgem. Chem.*, **275**, 320 (1954).
2. J. J. KATZ and E. RABINOWITCH, *The Chemistry of Uranium, Part I,* McGraw-Hill Book Company, Inc., New York (1951), p 337.

URANIUM-SILICON

THE CONSTITUTIONAL DIAGRAM

The constitutional diagram for the uranium-silicon system has been determined by Kaufmann [1] as shown in the accompanying figure. The formula U_3Si_2 is based upon work of Zachariasen [2], who also reports two forms of USi_2, one (beta USi_2) corresponding to the U_2Si_3 of Kaufmann. There is no disagreement about the compounds delta (U_3Si) [1, 2], zeta (USi) [1, 2], and iota (USi_3) [1-4]. However, Kaufmann [1] reports that delta (U_3Si) actually has a very narrow composition range near 23 a/o silicon, rather than a stoichiometric ratio of U_3Si.

CRYSTALLOGRAPHY

The data tabulated are from Zachariasen [2], except for iota (USi₃, which is from Kaufmann [1]. The discrepancies between these data and the constitutional diagram are explained above.

The structure of iota (USi₃) has been determined by others [3, 4] and is reported to be the L12-type, isomorphous with UGa₃, UIn₃, UGe₃, UPb₃, UAl₃, and USn₃ [3].

Zachariasen [2] reports that delta (U_3Si) is the only one of the intermetallic compounds in this system which does not have covalent bonds between silicon atoms and therefore is metallic in nature. This generalization presumably excludes USi_3, since Zachariasen did not report on it.
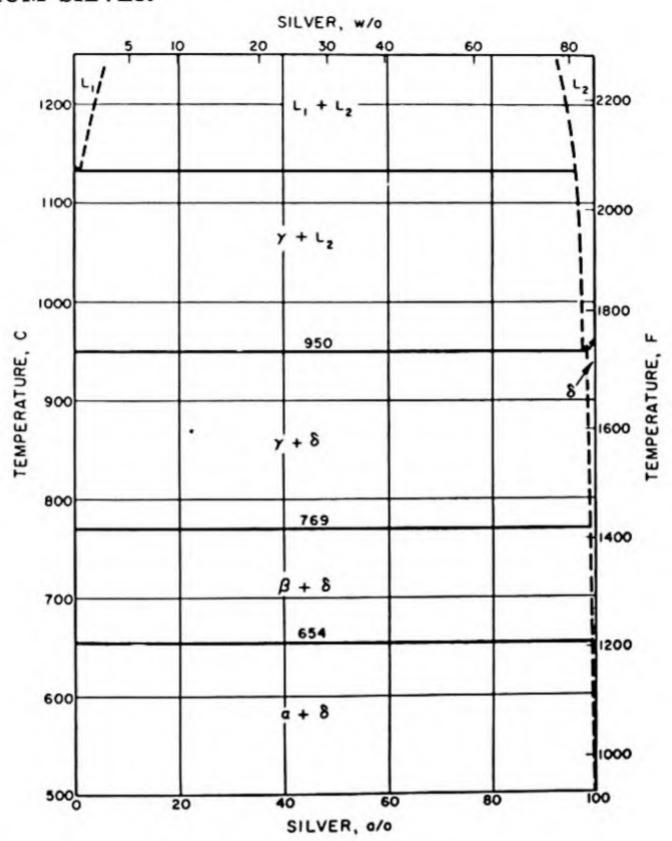
In epsilon (U_3Si_2) the silicon atoms are bonded together to form pairs normal to the fourfold axis. In zeta (USi), the silicon atoms are bonded together to form endless zigzag chains along the c-axis. In theta ("beta" USi_2), the silicon atoms form "graphite layers" normal to the sixfold axis; and in eta ("alpha" USi_2), a three-dimensional network of silicon atoms occurs, with uranium atoms in the interstices.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta (U_3Si)	Bc tetragonal	$a = 6.029$ ± 0.002 $c = 8.697$ ± 0.003	4	15.58		I4/mcm	
Epsilon (U_3Si_2)	Tetragonal	$a = 7.3298$ ± 0.0004 $c = 3.9003$ ± 0.0005	2	12.20		P4/mbm	
Zeta (USi)	Ortho-rhombic	$a = 5.66$ ± 0.01 $b = 7.67$ ± 0.01 $c = 3.91$ ± 0.01	4	10.40		Pbnm	Isomorphous with FeB
Eta ("alpha" USi_2)	Bc tetragonal	$a = 3.98$ ± 0.03 $c = 13.74$ ± 0.08	4	8.98		I4/amd	Isomorphous with $ThSi_2$, $PuSi_2$, $CeSi_2$, and $NpSi_2$
Theta ("beta" USi_2)	Hexagonal	$a = 3.86$ ± 0.01 $c = 4.07$ ± 0.01	1	9.25		P6/mmm	Isomorphous with AlB_2 and TiB_2
Iota (USi_3)	Cubic	$a = 4.03$	1	8.15		Pm3m	L12-type, $AuCu_3$ ordered structure

References

1. A. R. KAUFMANN, B. D. CULLITY and G. BITSIANES, "Uranium Silicon Alloys," *J. Metals*, 9, 23–27 (January, 1957).

2. W. H. ZACHARIASEN, "The Crystal Structure of Uranium Silicides and of $CeSi_2$, $NpSi_2$, and $PuSi_2$" (AECD-2092), *Acta Cryst.*, 2, 94–99 (1949).

3. J. T. MASKREY and B. R. T. FROST, "The System Uranium-Lead" (AERE-M/R 1027), *J. Inst. Metals*, 82 (4), 171–80 (1953).

4. ALDO IANDELLI and RICARDO FERRO, *Ann. chim.* (Rome), 42, 598–606 (1952).

URANIUM-SILVER

SILVER, w/o

SILVER, a/o

The Constitutional Diagram

Early work on the uranium-silver system [1, 2] indicated that uranium and silver are immiscible in the liquid state. More recently, the diagram has been mapped out rather thoroughly by Buzzard and co-workers [3].

The accompanying diagram is from the work of Buzzard [3]. The monotectic reaction is reported at 1132 C, on the basis of a uranium melting point of 1133 C. Buzzard reports the monotectic composition to be about 0.23 w/o silver at 1132 C, while Wilhelm reports it to be about 0.05 w/o silver [4]. Work from the United Kingdom reports the monotectic at 0.28 w/o silver [2].

The eutectic at the silver-rich end occurs at about 94.5 w/o silver and 950 C [3], although another report indicates that it occurs at about 15 a/o uranium [2].

The maximum solubility in silver is between 0.1 and 0.4 w/o uranium. Because there is no appreciable solubility of silver in uranium, silver has little effect on the uranium transformation temperatures [3].

CRYSTALLOGRAPHY

There are no intermetallic compounds in the uranium-silver system.

References

1. H. W. RUSSELL, unpublished information (December, 1944).
2. National Physical Laboratory, United Kingdom, unpublished information (May, 1949).
3. R. W. BUZZARD, D. P. FICKLE and J. J. PARK, "The Silver-Uranium System" (AECD-3600), *J. Research Natl. Bur. Standards*, **52** (3), 149–52 (1954).
4. H. A. WILHELM and O. N. CARLSON, "Uranium Alloy Newsletter" (May, 1954).

URANIUM-SODIUM

The solubility of uranium in liquid sodium at 97.8 C is reported to be less than 0.05 w/o and may be many times smaller [1]. Uranium and sodium in contact for long periods of time at 550 C showed no evidence of reaction [2].

CRYSTALLOGRAPHY

Probably there are no compounds in this system.

References

1. T. B. DOUGLAS, "A Cryoscopic Study of the Solubility of Uranium in Liquid Sodium at 97.8 C," *J. Research Natl. Bur. Standards*, **52**, 223–26 (1954).
2. AERE, United Kingdom, unpublished information (May, 1957).

URANIUM-SULFUR

The existence of four basic sulfides of uranium has been reported, US, U_5S_3, U_2S_3, and US_2 [1–4]. Zachariasen reports these compounds have well-defined formulas.

The melting point of US has been reported as greater than 2000 C, while that of US_2 has been reported as 1850 ± 100 C [3].

US_2 decomposes to U_2S_3 in a vacuum at 1300 C [5]. At 1530 C, the decomposition product of US_2 is reported to be U_5S_3 [6].

Various reports indicate that US_2 exists in two forms [5, 7, 8]. The transition temperature from the orthorhombic to tetragonal form is reported to be about 1350 C. Below this temperature, the two forms can coexist [7].

Additional discussion is available [8].

CRYSTALLOGRAPHY

The crystallography of the compounds US, U_5S_3, U_2S_3, "alpha" US_2, and "beta" US_2 is tabulated below. The data for U_5S_3, U_2S_3, and beta US_2 are from Picon [4, 7] while the data for US and alpha US_2 are from Zachariasen [1]. Picon [7] gives the following for alpha US_2: orthorhombic; $a = 4.12$, $b = 7.11$, $c = 8.46$ A; density, 8.07 ± 0.06 g/cm^3. Data for U_2S_3 are given by Zachariasen [1] as follows: orthorhombic; $a = 10.41$, $b = 10.65$, $c = 3.89$ A; density, 8.78 g/cm^3.
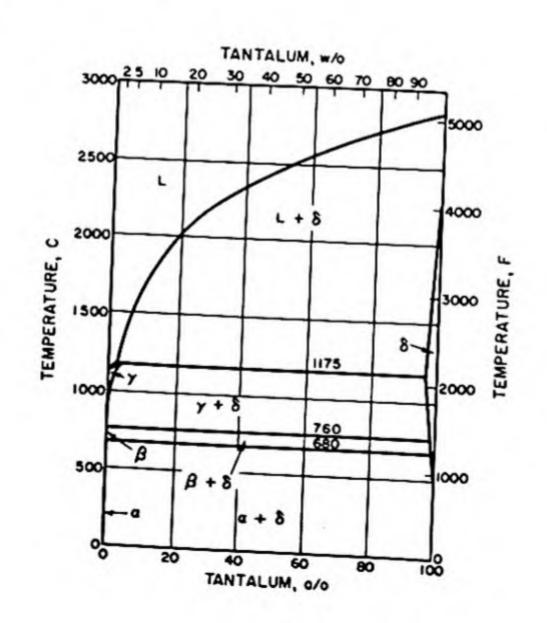
A subsulfide has been reported by Zumbusch [9]. Zachariasen [2] attributes this report to UOS, which has been found to have a tetragonal structure with $a = 3.835 \pm 0.001$ and $c = 6.681 \pm 0.001$ A, with a density of 9.60 g/cm^3. The UOS structure is the PbFCl-type with a P4/nmm space group.

Phase	Unit cell			Density, g/cm^3		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
US	Bcc	$a = 5.484$ ± 0.002	4	10.87			NaCl-type structure soluble with ThS and CeS
U_5S_3	Ortho-rhombic	$a = 7.41$ ± 0.02 $b = 8.06$ ± 0.02 $c = 11.70$ ± 0.03	4	8.31	8.30 ± 0.05		
U_2S_3	Ortho-rhombic	$a = 10.34$ ± 0.02 $b = 10.58$ ± 0.02 $c = 3.855$ ± 0.004	4	9.01	8.94 ± 0.07	Pbnm	Sb_2S_3-type structure; isomorphous with Np_2S_3 and Th_2S_3
"Alpha" US_2	Ortho-rhombic	$a = 4.22$ ± 0.02 $b = 7.08$ ± 0.04 $c = 8.45$ ± 0.04	4	7.90		Pmnb	Isomorphous with ThS_2
"Beta" US_2	Tetrag-onal	$a = 10.26$ $c = 6.30$			7.60 ± 0.06		

References

1. W. H. Zachariasen, "Crystal Structure of Sulfides and Oxy-sulfides of Uranium, Thorium, and Cerium," AECD-2141 (September 11, 1946).

2. W. H. Zachariasen, "Crystal Chemical Studies of the 5-f Series Elements, X. Sulfides and Oxy-sulfides," *Acta Cryst.*, **2**, 291–96 (1949).

3. E. D. Eastman, L. Brewer and L. Bromley, "Preparation and Properties of the Sulfides of Thorium and Uranium," *J. Am. Chem. Soc.*, **72**, 4019–23 (1950).

4. M. Picon and J. Flauhaut, "The Properties of Uranium Sulfides S_5U_3 and S_3U_2," *Compt. rend.*, **240**, 784–85 (1955).

5. M. Picon and J. Flauhaut, "Properties of the Sulfides of Uranium US_2, Alpha and Beta," *Compt. rend.*, **237**, 1160–62 (1953).

6. M. Picon and J. Flauhaut, "Uranium Sulfides," *Compt. rend.*, **240**, 535–36 (1955).

7. M. Picon and J. Flauhaut, "Dimorphism of the Sulfide of Uranium, US_2," *Compt. rend.*, **237**, 808–10 (1953).

8. J. J. Katz and E. Rabinowitch, *The Chemistry of Uranium, Part I*, McGraw-Hill Book Company, Inc., New York (1951), pp. 330–35.

9. M. Zumbusch, "The Structure of Uranium-Subsulfide and of the Subsulfides of Iridium and Rhodium," *Z. anorg. u. allgem. Chem.*, **243**, 322–29 (1940).

URANIUM-TANTALUM

THE CONSTITUTIONAL DIAGRAM

Early work by Ahmann [1] indicated that no intermetallic compounds exist in the uranium-tantalum system and that a peritectic reaction occurs at the uranium end of the system. Schramm, Gordon, and Kaufmann [2] studied the system more intensively and established the constitutional diagram as shown.

Both tantalum and tungsten form peritectic systems with limited solid solutions. In the case of tantalum, the peritectic temperature is 1175 C. The solubility of tantalum in uranium and of uranium in tantalum is probably less than 2 a/o [2].

A ternary carbide, approximating $UTa_{10}C_4$, was observed which is more stable than the carbides of either uranium or tantalum alone. This carbide is of low symmetry but the structure is undetermined [2]. A second ternary carbide is reported to be face-centered cubic with $a = 4.41$ A.

Data from the United Kingdom support the general features of the system uranium-tantalum [3].

CRYSTALLOGRAPHY

There are no intermetallic compounds in the uranium-tantalum system.

References

1. D. H. AHMANN, unpublished information (March, 1946).
2. C. H. SCHRAMM, A. R. GORDON and A. R. KAUFMANN, "The Alloy Systems Uranium-Tungsten, Uranium-Tantalum, and Tungsten-Tantalum" (AECD-2686), *J. Metals*, **2**, (1949).
3. Atomic Energy Research Establishment, United Kingdom, unpublished information (1954).

URANIUM-TELLURIUM

The uranium-tellurium system is incompletely known; however, Ferro reports the compounds UTe, U_3Te_4, U_2Te, and UTe_2, in addition to a phase of higher tellurium content.[1] The latter phase may correspond to the $UTe_{2.2}$ described by Montignie.[2] Katz and Rabinowitch, in an earlier review of the system, concluded that UTe, U_2Te_3, and $UTe_{2.2}$ were among the compounds found in the system.[3]

CRYSTALLOGRAPHY

The structures below for UTe, U_3Te_4, and UTe_2 are from Ferro [1].

Phase	Unit cell			Density, g cm³		Space group	Remarks
	Type	Dimensions, Å	Number of molecules	X-ray	Other		
UTe	Cubic	$a = 6.163$	4	10.37			NaCl-type structure
U_3Te_4	Cubic	$a = 9.397$	4			$I\bar{4}3d$	Th_3P_4-type structure
UTe_2	Tetragonal	$a = 4.006$ $c = 7.471$					

References

1. R. FERRO, "Certain Uranium-Selenium and Uranium-Tellurium Compounds," *Z. anorg. u. allgem. Chem.*, **275**, 320 (1954).
2. E. MONTIGNIE, *Bull. soc. chim.* (France), 748–49 (1947).
3. J. J. KATZ and E. RABINOWITCH, *The Chemistry of Uranium, Part I*, McGraw-Hill Book Company, Inc., New York (1951), p 337.

URANIUM-TERBIUM

Uranium and terbium exhibit an immiscibility gap in the liquid state. Solubility of terbium in liquid uranium is reported to increase from 0.2 w/o at 1150 C to 0.4 w/o at 1250 C [1].

CRYSTALLOGRAPHY

Nothing is known concerning the possibility of compounds in this system.

Reference

1. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.

URANIUM-THALLIUM

An intermetallic compound, UTl_3, has been reported.[1] Solubility of uranium in liquid thallium is reported to increase from 0.12 w/o at 800 C to 0.17 w/o at 900 C.

CRYSTALLOGRAPHY

The tabulated data for UTl_3 are from the work of Iandelli and Ferro [1].

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
UTl_3	Simple cubic	$a = 4.675$	1			Pm3m	Isomorphous with UGa_3, UIn_3, USi_3, UGe_3, and UPb_3

References

1. ALDO IANDELLI and RICARDO FERRO, *Ann. chim* (Rome), **42**, 598–608 (1952).

2. E. E. HAYES and P. GORDON, *J. Met. and Cer.*, TID-65, 130–41 (July, 1948). Classified.
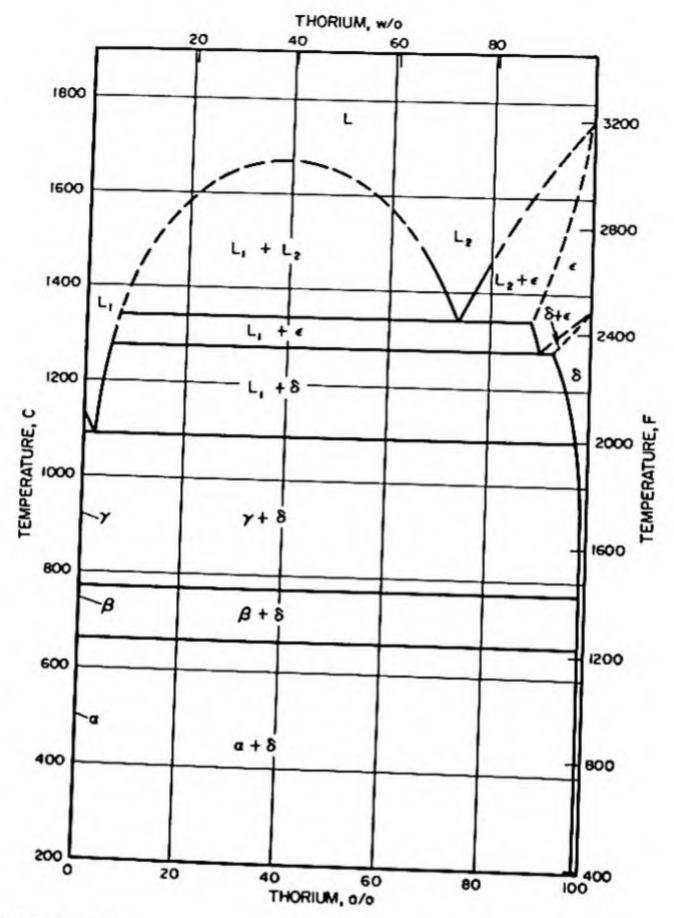
URANIUM-THORIUM

THE CONSTITUTIONAL DIAGRAM

The diagram shown is based upon the work of Carlson [1, 2], modified to include the results of Bentle [3] at the high-thorium end of the system. The general characteristics are confirmed by Murray [4], except that the immiscibility gap is reported to extend from 6 to 50 a/o thorium.

Solubility of thorium in uranium is very limited, being 0.30 a/o thorium at 900 C and less than 0.5 a/o thorium at 700 C [4].

The details of the high-thorium portion of the system were determined by electrical-resistivity measurements and room-temperature x-ray lattice-parameter measurements. Solubility of uranium in thorium is given as being 0.7, 1.1, 1.1, 1.8, and 2.7 w/o at 25, 600, 800, 1000, and 1100 C [3]. Bauer [5] gives values of 0.7, 0.7, and 1.75 w/o uranium at 800, 900, and 1000 C, while Murray reports values of 1.0 and 2.45 a/o at 800 and 1300 C, respectively. Wilson [6] reports slightly higher values, giving 2.5, 4.5, and 7.5 w/o uranium at 950, 1150 and 1250 C on the basis of high-temperature x-ray measurements.

CRYSTALLOGRAPHY

There are no intermetallic compounds in the system uranium-thorium.

References

1. O. N. CARLSON, "Some Studies of the Uranium-Thorium-Zirconium Ternary Alloy System," AECD-3206 (June 5, 1950).

2. O. N. CARLSON and A. H. DAANE, "The Tuballoy-Thorium Binary System," CT-2717 (April, 1945).

3. G. G. BENTLE, "A Physical Metallurgical Study of Thorium-Rich Thorium-Uranium Alloys," NAA-SR-2069 (January 15, 1958).

4. J. R. MURRAY, United Kingdom, unpublished information (1957).

5. A. A. BAUER, F. A. ROUGH and R. F. DICKERSON, "An Investigation of Uranium Solid Solubility in Thorium," BMI-1188 (May 29, 1957).

6. W. B. WILSON, A. E. AUSTIN and C. M. SCHWARTZ, "The Solid Solubility of Uranium in Thorium and the Allotropic Transformation of Thorium-Uranium Alloys," BMI-1111 (July 12, 1956).

URANIUM-THULIUM

Uranium and thulium exhibit an immiscibility gap in the liquid state. Solubility of thulium in liquid uranium is reported to increase from 0.025 w/o at 1150 C to 0.075 w/o at 1250 C [1].
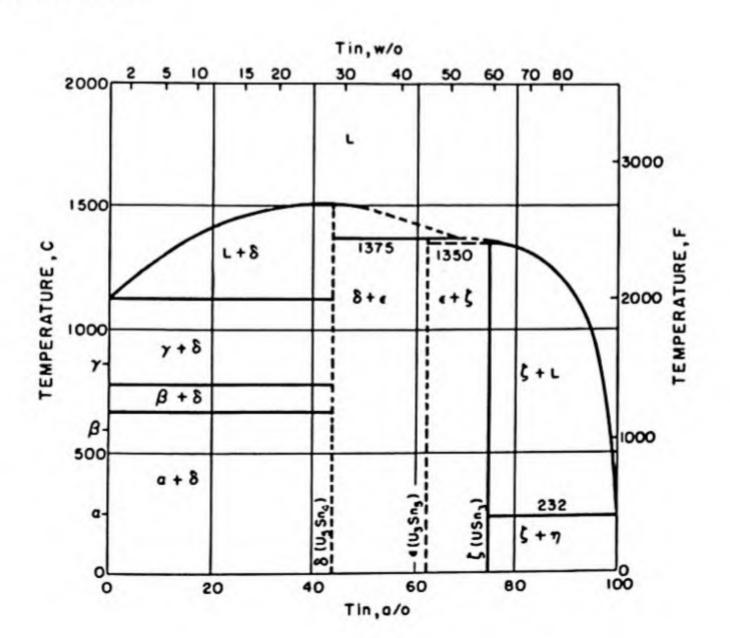
CRYSTALLOGRAPHY

Nothing is known concerning the possibility of compounds in this system.

Reference

1. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.

URANIUM-TIN

THE CONSTITUTIONAL DIAGRAM

The diagram shown was determined by Treick and associates [1]. Except for USn_3, the compound compositions are not accurately known because of the pyrophoricity of these compounds and the consequent difficulty in handling [2]. The diagram is based on the result of metallographic examination, thermal analysis, and x-ray diffraction.

The USn_3 has also been reported by Maskrey [3].

CRYSTALLOGRAPHY

Data are available only for USn_3. The data in the table are from Rundle [2]. Maskrey reports similar information, giving a value $a = 4.626$ A. It is an ordered phase and is reported to be isomorphous with UAl_3, UGa_3, UIn_3, USi_3, and UPb_3.[3]

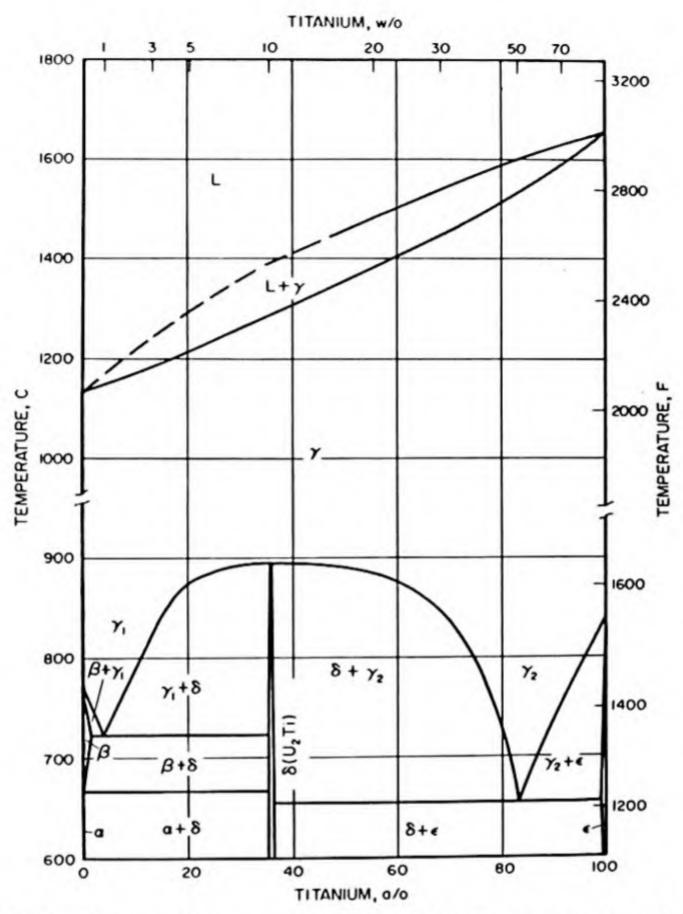| Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
USn_3	Simple cubic	$a = 4.63$	1	9.95		Pm3m	L12-type, AuCu₃ ordered structure; isomorphous with UAl₃

References

1. D. A. TREICK, J. H. CARTER, A. I. SNOW, R. R. BALDWIN and A. S. WILSON, "The Uranium-Tin System," M-3107 (1945).
2. R. E. RUNDLE and A. S. WILSON, "The Structure of Some Metal Compounds of Uranium" (AECD-2388), *Acta Cryst.*, 2, 148–50 (1949).
3. J. T. MASKREY and B. R. T. FROST, "The System Uranium-Lead," (AERE M/R 1027), *J. Inst. Metals*, 82 (4), 171–80 (1953).

URANIUM-TITANIUM

THE CONSTITUTIONAL DIAGRAM

The diagram shown is from Knapton [1] and is in essential agreement with the work of Udy and Boulger [2]. The principal differences are in reported solubilities of titanium in the alpha- and beta-uranium phases and in the solubility range of the delta (U_2Ti) phase. Udy and Boulger report maximum values for titanium solubility in the alpha and beta phases as 4 and 3 a/o, respectively [2]. Knapton reports that impurities are gettered by initial titanium additions resulting in apparently large solubility values; values of less than 1 a/o and 1½ a/o are given for alpha and beta solubilities [1]. Knapton, in performing a detailed study of the

delta (U_2Ti) phase region, reports [1] a very limited range of solubility for U_2Ti on the basis of both metallographic and x-ray studies, which showed that little change in parameter values was observed with change in composition in the vicinity of the delta phase. Udy and Boulger had reported [2] a solubility range for the delta (U_2Ti) phase of from about 28 to 42 a/o titanium.

Early reports of a peritectic reaction at the uranium end of the system are undoubtedly in error.[3]

Minor differences in remaining features of the diagram have been reported. Knapton [1] places the gamma eutectoid at 4 a/o titanium and 723 C. Udy [2] reports 6.0 a/o and 718 C for the same point. The eutectoid at the titanium end of the system has been reported as 83 a/o titanium by Knapton [1], 72 a/o titanium by Udy [2], and 77 a/o titanium by Sey-

bolt [4]. Impurities, notably oxygen and nitrogen, are undoubtedly responsible for at least part of the variations in reported values.

The solubility of uranium in epsilon (alpha titanium) is reported as about 0.8 a/o at 655 C [1].

CRYSTALLOGRAPHY

The data tabulated below are from Knapton [5]. Similar data have been reported by Tucker [6], giving $a = 4.826$ A and $c = 2.852$ A.

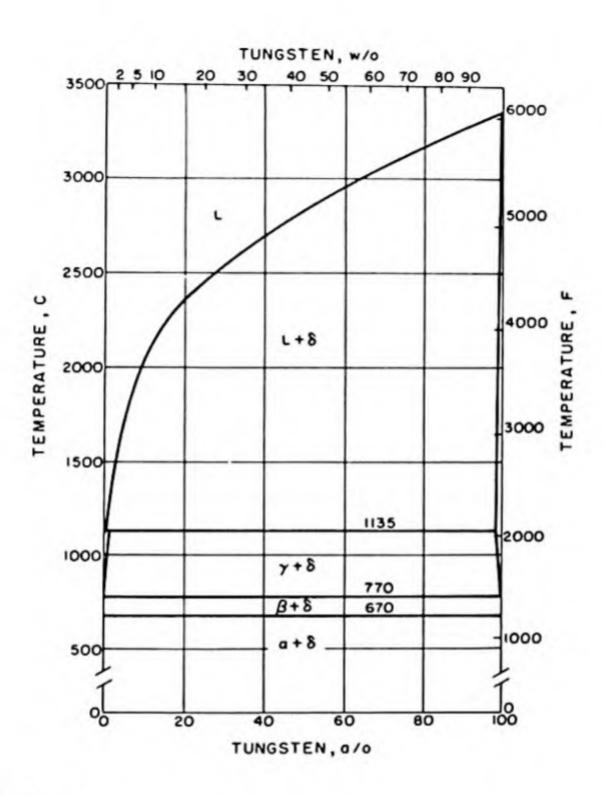| Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta (U₂Ti)	Hexagonal	$a = 4.828$ $c = 2.847$	1			P6 mmm	C32-type; isostructural with AlB₂

References

1. A. G. KNAPTON, "The System Uranium-Titanium," *J. Inst. Metals*, **83**, 497 (1954–55).
2. M. C. UDY and F. W. BOULGER, "Uranium-Titanium Alloy System," *Trans. AIME*, **200**, 207–10 (1954).
3. R. W. BUZZARD, R. B. LISS and D. P. FICKLE, "Titanium-Uranium System in the Region Zero to Thirty Atomic Per Cent Titanium" (AECD-3418), *J. Research Natl. Bur. Standards*, **50**, 209–14 (1953).
4. A. U. SEYBOLT, D. W. WHITE, F. W. BOULGER and M. C. UDY, "Tentative Uranium-Titanium Phase Diagram," TID-71, 118–19 (1951).
5. A. G. KNAPTON, *Acta Cryst.*, **7**, 457 (1954).
6. C. W. TUCKER, JR., Knolls Atomic Power Laboratory, unpublished information (1950).

URANIUM-TUNGSTEN

THE CONSTITUTIONAL DIAGRAM

The constitutional diagram of the uranium-tungsten system is similar to that of the uranium-tantalum system. A peritectic reaction occurs at the uranium end of the system, although the temperature of the peritectic is only slightly above the melting point of uranium [1].

Schramm, Gordon, and Kaufmann report that the solubility of uranium in tungsten and of tungsten in uranium is less than 1 a/o.[1] Recent reports from the United Kingdom are in agreement and give solubilities of 0.2 to 0.5 a/o tungsten [2] and 0.4 to 0.7 a/o tungsten in uranium at 1000 C. A solubility of 0.1 a/o uranium in tungsten at 1000 C is also reported [3].
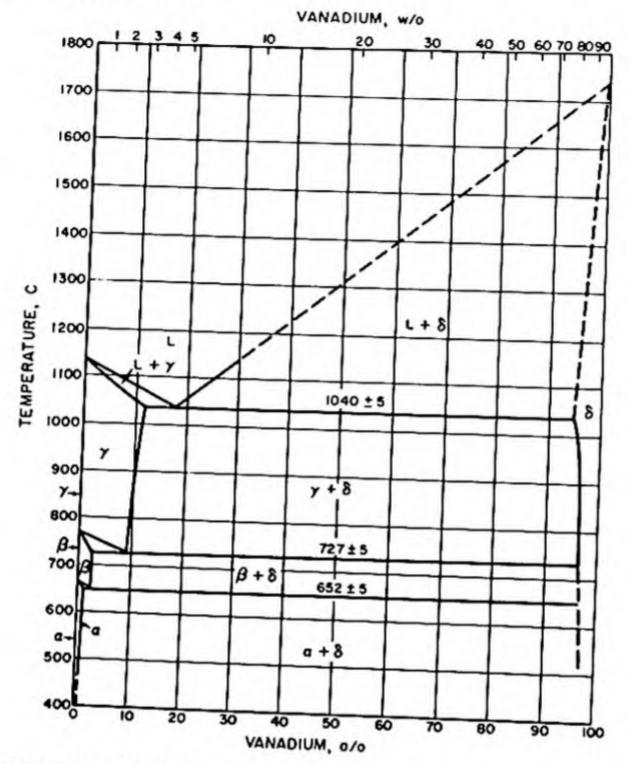
CRYSTALLOGRAPHY

There are not intermetallic compounds in the system uranium-tungsten.

References

1. C. H. SCHRAMM, P. GORDON and A. R. KAUFMANN, "The Alloy Systems Uranium-Tungsten, Uranium-Tantalum, and Tungsten-Tantalum" (AECD-2686), *J. Metals*, **188**, 195–204 (1950).

2. National Physical Laboratory, United Kingdom, unpublished information (October, 1948).

3. D. SUMMERS-SMITH, "The System Uranium-Tungsten," *J. Inst. Met.*, **83**, 383 (1954–1955).

URANIUM-VANADIUM

VANADIUM, w/o

THE CONSTITUTIONAL DIAGRAM

The diagram as shown was determined by Saller and Rough [1]. The solubility in the gamma was found to be a maximum of about 12 a/o vanadium at the eutectic and 9 a/o vanadium at the 727 C eutectoid. The solubility in the beta is about 2 a/o vanadium and in the alpha less than 1.5 a/o vanadium. The solubility of uranium in vanadium is limited at all temperatures, with a maximum value of about 4 a/o uranium at 1040 C.

The diagram was determined principally by thermal analysis and metallography, and the absence of intermetallic compounds was confirmed by x-ray diffraction.

Seybolt [2] has reported that an allotropic modification of vanadium occurs at 1550 C. This conclusion is based on thermal and thermoelectric measurements. McCaldin and Duwez [3] did not find evidence of the modification by thermal analysis. Saller and Rough examined vanadium by

thermal analysis, but did not go above 1200 C. Since it has not been confirmed, the proposed modification has not been incorporated into the diagram.

CRYSTALLOGRAPHY

There are no intermetallic compounds in the system uranium-vanadium.

References

1. H. A. SALLER and F. A. ROUGH, "Vanadium-Uranium Constitutional Diagram," *J. Metals,* **15,** 545–48 (April, 1953).
2. A. U. SEYBOLT and H. T. SUMSION, "Vanadium-Oxygen Solid Solutions," *J. Metals,* **5,** 292–99 (February, 1953).
3. J. O. McCALDIN and POL DUWEZ, "Allotropic Transformations at High Temperature," *J. Metals,* **6,** 619–20 (May, 1954).

URANIUM-YTTERBIUM

Uranium and ytterbium show little miscibility in the liquid state. The solubility of ytterbium in liquid uranium is reported to be 0.15 w/o at 1150 C and 0.2 w/o at 1250 C, while uranium solubility in ytterbium is essentially nil at 1000 C and 0.8 w/o at 1250 C.

CRYSTALLOGRAPHY

Data concerning the possibility of compounds in this system are not available.

Reference

1. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.

URANIUM-YTTRIUM

Uranium and yttrium exhibit an immiscibility gap in the liquid state. Solubility of yttrium in liquid uranium is reported to increase from 0.075. w/o at 1150 C to 0.15 w/o at 1250 C [1].
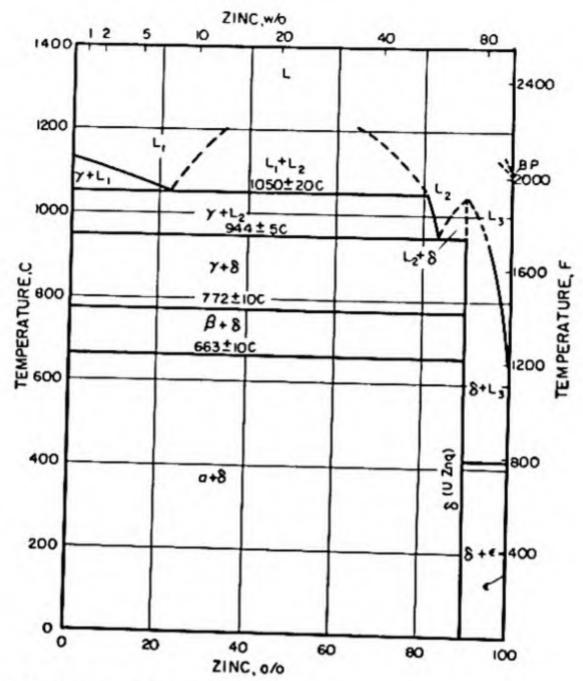
CRYSTALLOGRAPHY

Nothing is known concerning the possibility of compounds in this system.

Reference

1. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.

URANIUM-ZINC

THE CONSTITUTIONAL DIAGRAM

The constitution of uranium-zinc alloys has been determined by Chiotti, Klepfer, and Gill [1] from x-ray, metallographic, thermal, and vapor-pressure data. The diagram shown is the one determined at 5-atm pressure.

The solubility of zinc in uranium is very low, undetectable by the experimental methods employed. Solubilities of uranium in zinc at various temperatures are given below:

Temperature, C	Uranium, w/o
419	0.025
450	0.20 ± 0.1
500	0.28 ± 0.01
550	0.30 ± 0.08
600	0.45 ± 0.02
650	1.3 ± 0.2
700	3.1 ± 0.3

At 910 C the solubility of uranium in zinc was calculated to be 14.6 a/o uranium.

The diagram shown is identical up to 910 C to the one determined at 1-atm pressure. Under the lower pressure condition, zinc boils at 910 C and the compound UZn_9 decomposes at 945 ± 3 C to the zinc vapor and liquid of approximate eutectic composition. Above 947 C, zinc vapor and the uranium gamma and liquid phases exist in equilibrium.

CRYSTALLOGRAPHY

Only one compound forms in this system, analytical and metallographic data indicating a composition of UZn_9. The compound is believed to be hexagonal.

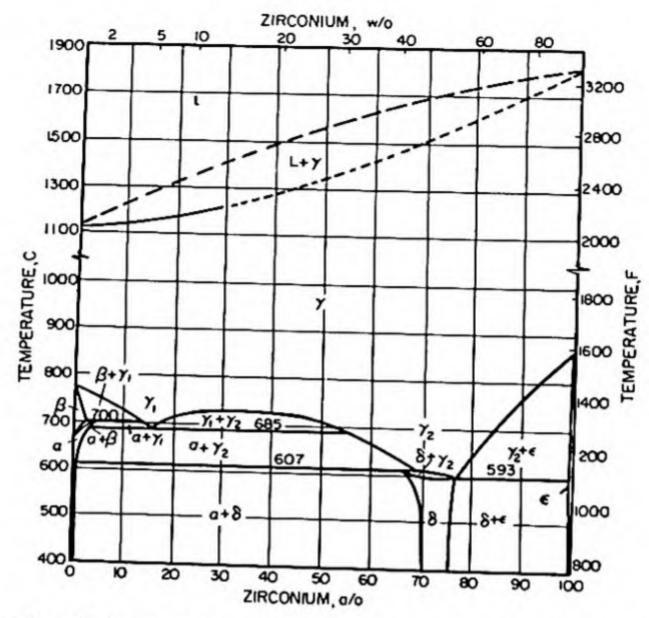| Phase	Unit cell			Density, g/cm^3		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta (UZn_9)	Hexag-onal	$a = 8.99$ $c = 8.98$				P6/mmm	

Reference

1. P. CHIOTTI, H. H. KLEPFER and K. J. GILL, "Uranium-Zinc System," *J. Metals,* **9,** 51-57 (January, 1957).

URANIUM-ZIRCONIUM

THE CONSTITUTIONAL DIAGRAM

The system uranium-zirconium has been studied by a number of investigators. The diagram shown is based largely on the work of Saller [1] and Rough [2], but the principal features of the system were reported earlier by Kaufmann [3] and Peterson [4]. The diagram is based on work with alloys prepared by arc melting selected biscuit uranium and Grade I crystal-bar zirconium.

There is agreement that complete solid solution exists between gamma uranium and beta zirconium [1–6], but there was some question concerning the stability of the intermediate epsilon phase. However, results of studies by Bauer [2], Kearns [7], and Holden [8] confirm the stability of the phase. Oxygen and nitrogen, in ternary alloy combination with the delta phase, have been shown [2] to cause its decomposition. Features shown

in this region of the diagram are based upon the work of Rough, Austin, Bauer, and Doig [2]. However, fairly wide variations in the solubility range of the delta phase have been reported.[7, 9, 10] Knapton [9] reports that delta forms peritectoidally at 620 C and 63 a/o zirconium, giving a solubility range of 63 to 79.5 a/o zirconium at 600 C and a solubility range of 66 to 79 a/o zirconium at 500 C. Studies in this region are complicated by the pronounced effect of oxygen and nitrogen on the delta-phase solubility limits and by the nature of the gamma-to-delta transformation in this region. Thus, supersaturated delta forms during low-temperature annealing of initially gamma-quenched alloys containing from about 50 to 90 a/o zirconium. Rejection of either alpha uranium or alpha zirconium from the supersaturated delta phase to yield the equilibrium delta composition occurs during subsequent heat treatment at temperatures below 600 C, the rate of rejection decreasing rapidly with temperature and in compositions close to the delta-phase composition limits.[11]

The gamma-plus-epsilon region of the diagram has been studied by several investigators [1-5, 12], and variations in the gamma boundary values have been explained [2, 13] as arising from oxygen and nitrogen contamination. The value of solubility of uranium in alpha zirconium (0.3 a/o) at the isotherm was determined by McGeary [12] and was based on precision dilatometric measurements of a series of alloys.

The general features of the high-uranium end of the system have been

confirmed by a number of investigators.[1, 3, 4, 5, 14] Refinement of this area to include the gamma$_1$-plus-gamma$_2$ region is indicated by the more recent works.[1, 5] The details shown are based largely on the work of Saller, Rough, and Bauer [1], who have employed quantitative lineal analysis of metallographic samples, metallography, thermal analysis, and more recently high-temperature x-ray techniques [15] to establish the phase regions. However, Summers-Smith disagrees, reporting [5] dilatometric and high-temperature x-ray evidence for a beta-plus-gamma$_2$ field extending to 62 a/o zirconium in the temperature range 662 to 693 C, there being no alpha-plus-gamma$_1$ field.

The solubility of zirconium in beta uranium is reported by Summers-Smith [5] as 2.5 a/o and in alpha uranium as 1.5 a/o. Saller [1] reports values of about 3 and 5 a/o for maximum solubility, with solubility decreasing rapidly to less than 1 a/o below 660 C. Zegler [16] gives values between 0.5 and 1 a/o at 675, 700, and 750 C in the beta phase; between 0.25 and 0.5 a/o from 500 to 640 C; and slightly in excess of 0.5 a/o at 660 C in the alpha phase.

CRYSTALLOGRAPHY

The delta phase was reported by Holden to be an ordered structure, and subsequently large unit cells based on the gamma-uranium structure were reported, giving $a = 10.678$ A [17] and 10.69 A [18]. However, indexing is not altogether satisfactory, certain reflections having parameters slightly off the values necessary for a cubic structure. Therefore, Rough [2] suggested a hexagonal or rhombohedral pseudo-cubic structure with $a = 8.793$ and $c = 9.212$ at 575 C in a 72 a/o alloy. Adam [19] suggested that the discrepancies may arise from stacking faults; the delta-phase structure is strongly polarizing under a microscope, and a cubic structure is unlikely. Silcock [20] and, more recently, Boyko [21] and Mueller [22] determined the structure to be primitive hexagonal, accounting well for both the positions and intensities of the lines. This structure is partially ordered, with zirconium atoms located at the 0, 0, 0 position while zirconium and uranium atoms are located randomly at the $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$ positions. The random distribution of uranium and zirconium atoms allows a considerable range in composition. Silcock [20] and Boyko [21] report similar data for the phase as given below.

| Phase | Unit cell | | | Density, g/cm³ | | Space group | Remarks |
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Delta (UZr₂)	Hexag- onal	$a = 5.03$ $c = 3.08$	1		9.7	P6/mmm	Partially disordered C32-type AlB₂ structure

References

1. H. A. SALLER, F. A. ROUGH and A. A. BAUER, private communication (1954).

2. F. A. ROUGH, A. E. AUSTIN, A. A. BAUER and J. R. DOIG, "The Stability and Existence Range of the Zirconium-Uranium Epsilon Phase," BMI-1092 (May 28, 1956).

3. A. R. KAUFMANN, Technical Progress Report, MIT-1078 (April, 1952).

4. O. N. CARLSON and D. PETERSON, "Some Studies of the Uranium-Thorium-Zirconium Ternary Alloys System," AECD-3206 (June 5, 1950).

5. D. SUMMERS-SMITH, "The Constitution of Uranium-Zirconium Alloys," *J. Inst. Metals*, 83 (February, 1955).

6. N. S. KALISH, unpublished information (1953).

7. J. KEARNS, unpublished information (1956).

8. A. N. HOLDEN and W. E. SEYMOUR, "The Uranium-Zirconium System," *Trans. AIME*, 209, 515 (1957).

9. A. G. KNAPTON, United Kingdom, unpublished information (1957).

10. J. F. DUFFEY and C. A. BRUCH, "The Delta Phase Field of the Uranium-Zirconium Equilibrium Diagram," submitted to AIME for publication (1957).

11. A. A. BAUER, private communication (1957).

12. R. K. McGEARY, "Dilatometric Investigation of Zirconium, Zirconium-Uranium, Zirconium-Oxygen, and Zirconium-Nitrogen Alloys," WAPD-36 (July, 1951).

13. A. A. BAUER, G. H. BEATTY and F. A. ROUGH, "The Constitution of Zirconium-Uranium Alloys Containing Oxygen or Nitrogen," BMI-1187 (May, 1957).

14. R. W. BUZZARD, R. B. LISS and D. P. FICKLE, "The Uranium-Zirconium Binary System," *J. Met. and Cer.*, TID-2002 (August, 1952).

15. A. A. BAUER and A. E. AUSTIN, private communication (1956).

16. S. T. ZEGLER and L. T. LLOYD, Quarterly Report (Metallurgy Division), ANL-5489, 44–50 (March, 1956).

17. D. PETERSON, Quarterly Summary Research Report in Metallurgy, ISC-575 (July, 1955).

18. M. H. MUELLER, "The Delta Phase Found in U-Zr Alloys," *Acta Cryst.*, 8, 849–50 (1955).

19. J. ADAM, United Kingdon, unpublished information (1957).

20. J. M. SILCOCK, *Trans. AIME*, 209, 521 (1957).

21. E. R. BOYKO, "The Structure of the Phase in the Uranium-Zirconium System," *Acta Cryst.*, 10, 712 (1957).

22. M. H. MUELLER, H. W. KNOTT and L. HEATON, "The Hexagonal Phase Found in Certain Zirconium and Titanium Alloys," Presented at the 15th Pittsburgh Diffraction Conference (November 7, 1957).

URANIUM-ALUMINUM-SILICON

The region of the system which has been studied includes UAl_4, UAl_3, silicon, and uranium [1], but no diagram is available.

It is reported that 0.8 w/o silicon is sufficient to suppress the formation of UAl_4 entirely with a content of 20 w/o uranium. The phases in equilibrium then appear to be UAl_3, silicon, and aluminum [1]. However, the addition of up to 1 w/o silicon to alloys containing 40 and 50 w/o uranium was studied and found to depress the UAl_4 peritectic temperature to about 703 C, but apparently does not eliminate the phase. No noticeable effect of these additions on the liquidus of alloys in this range was observed [2].

The lattice constant of UAl_3 is altered by partial replacement of the aluminum atoms by silicon atoms. The composition $U(Al_{0.96} Si_{0.04})_3$ represents the average replacement, though actual replacement appears to be a function of temperature. No uranium was observed to be soluble in the aluminum and silicon phases; hence, the mutual solubilities of aluminum and silicon are unchanged.

No change could be detected either in the aluminum-silicon [1] or aluminum-rich uranium-aluminum [2] eutectic temperatures.

CRYSTALLOGRAPHY

No new phases are reported.

References

1. E. J. BOYLE, unpublished information (February, 1951).
2. V. W. STORHOK and A. A. BAUER, private communication (1958).

URANIUM-ALUMINUM-THORIUM

The aluminum-rich corner of this system has been studied.[1] The data indicate a ternary eutectic in the neighborhood of 76 w/o aluminum, 18 w/o to thorium, and 6 w/o uranium. The products of the eutectic decomposition are thought to be aluminum, UAl_3, and $ThAl_3$.
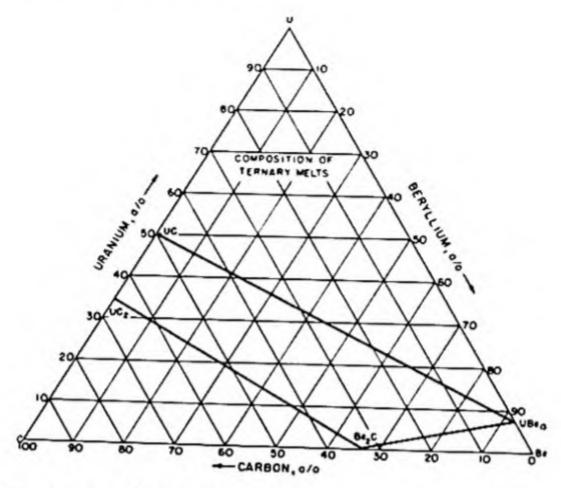
CRYSTALLOGRAPHY

No compounds not appearing in the binary system were detected.

Reference

1. G. E. BOBECK and H. A. WILHELM, "Alloys of Aluminum, Thorium, and Uranium," ISC-832 (December, 1956).

URANIUM-BERYLLIUM-CARBON

THE CONSTITUTIONAL DIAGRAM

A trapezoidal region, outlined in the diagram, has been studied.[1] No new phases were discovered in this area of the system. It is uncertain whether an additional line dividing the trapezoid into triangles should be drawn between UC and Be_2C or between UC_2 and UBe_{13}.

The analyzed compositions of the alloys and results of examination by x-ray diffraction are given below. The system has also been studied at the National Bureau of Standards, but the resulting data were not available for publication.

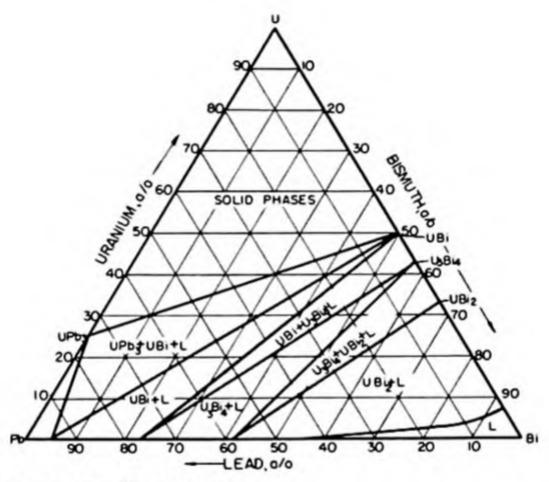| Composition, a/o			Phases identified
U	C	Be	
10.8	22.1	67.2	$UC - Be_{13}U$
8.4	32.5	59.1	$UC + UC_2$
21.2	40.3	38.4	UC
5.5	32.0	62.5	$UC + Be_2C$
21.9	29.9	48.2	$UC + Be_{13}U$
27.5	35.0	37.5	$UC + UC_2$
11.0	41.8	47.1	UC_2
21.3	42.2	36.5	UC_2
28.7	49.4	21.9	$UC_2 + UC$
34.8	60.8	4.4	UC_2

CRYSTALLOGRAPHY

No new phases have been reported.

Reference

1. A. R. KAUFMANN, P. A. KULIN and L. R. ALLEN, unpublished information (1949).

URANIUM-BISMUTH-LEAD

THE CONSTITUTIONAL DIAGRAM

A portion of the uranium-bismuth-lead system has been studied by Teitel [1]. The 800 C isothermal section shown [2] represents a revision of this work to include the recently identified U_3Bi_4 phase.

It is seen that the three uranium-bismuth compounds exist in equilibrium with liquid phases containing up to about 95 a/o lead. The UPb_3 phase exists in equilibrium with UBi and liquid containing less than 5 a/o bismuth.
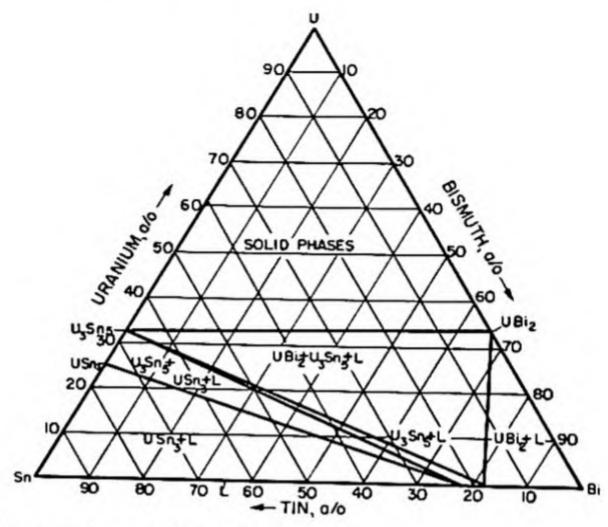
CRYSTALLOGRAPHY

No new phases have been reported.

References

1. R. J. TEITEL, O. F. KAMMERER and D. H. GURINSKY, unpublished information (August 31, 1951).
2. R. J. TEITEL and J. S. BRYNER, private communication (1956).

URANIUM-BISMUTH-TIN

THE CONSTITUTIONAL DIAGRAM

The portion of the diagram shown is from Teitel [1] and is drawn for a temperature of 350 C.

Tin lowers the solubility of uranium in the liquid phase. The tin compounds exist in equilibrium with liquids containing less than 82 a/o bismuth.
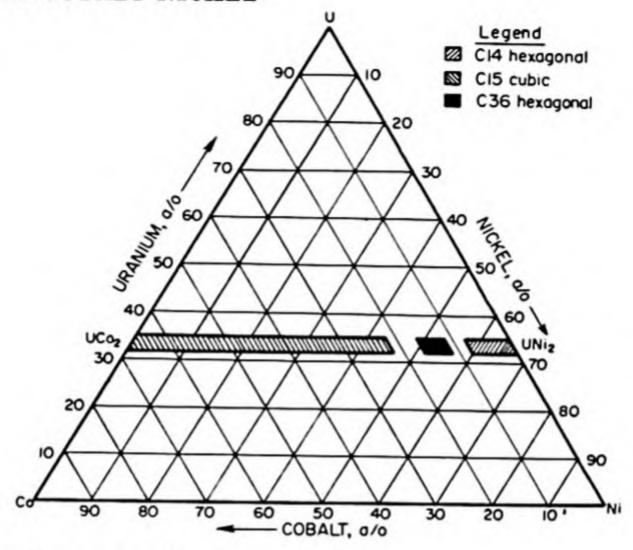
CRYSTALLOGRAPHY

No new phase has been reported.

Reference

1. R. J. TEITEL, private communication (1956).

URANIUM-COBALT-NICKEL

Legend
- ▨ C14 hexagonal
- ▧ C15 cubic
- ■ C36 hexagonal

THE CONSTITUTIONAL DIAGRAM

The pseudo binary UCo_2-UNi_2 has been studied [1]. The compound UCo_2 has the C15-type structure while the compound UNi_2 has the C14-type structure. Isotherms at 700 and 900 C show similar phase fields. The diagram shown is for 900 C. An intermediate phase X occurs with the C36-type structure, and in some alloys an additional pattern was observed. Work with single crystals showed the pattern to be the result of a large c-spacing. The structure could not be reproduced in samples of the same nominal composition.

Solubility limits are given as:

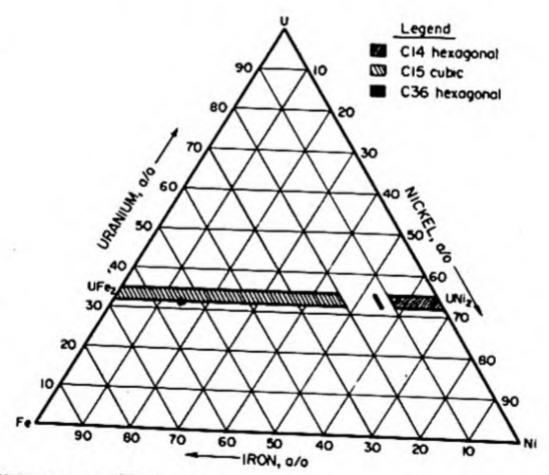|	900 C		700 C	
	Nickel, a/o	Cobalt, a/o	Nickel, a/o	Cobalt, a/o
$UNi_2/(UNi_2 + X)$	58.5	8.2	56.3	10.4
$X/(UNi_2 + X)$	55.6	11.1	55.6	11.1
$X/(X + UCo_2)$	50.7	16.0	50.7	16.0
$UCo_2/(X + UCo_2)$	45.3	21.4	45.2	21.5

CRYSTALLOGRAPHY

The structure of UCo_2 and UNi_2 has been given by Baenziger [2], but for consistency, all the parameters here, including that of the X-phase are taken from Brooks [1].

Phase	Unit cell			Density, g/cm^3		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
UCo₂	Fcc	$a = 7.0051$	8	13.8		Fd3m	C15 MgCu₂ structure
UNi₂	Hexagonal	$a = 4.959$ $c = 8.245$	4	13.5		P6₃ mmc	C14 MgZn₂ structure
X	Hexagonal	$a = 4.963$ $c = 16.395$	8	—		P6₃/mmc	C36 MgNi₂ structure

References

1. G. B. BROOKS, G. I. WILLIAMS and E. A. SMITH, "Pseudo-Binary Phase Sections Between Laves Phases in Ternary Alloys of Uranium," *J. Inst. Met.*, **83**, 271 (1954–55).

2. N. C. BAENZIGER, R. E. RUNDLE, A. I. SNOW and A. S. WILSON, "Compounds of Uranium With the First Long Period" (AECD 2598), *Acta Cryst.*, **3**, 34 (1950).

URANIUM-IRON-NICKEL

THE CONSTITUTIONAL DIAGRAM

The pseudo binary UFe₂-UNi₂ has been studied [1]. The compound UFe₂ has the C15-type structure while the compound UNi₂ has the C14-type structure. Isotherms at 700 and 900 C show similar phase fields. The diagram shown is for 900 C. An intermediate phase X occurs with the C36-type structure.

Solubility limits are given as:

	900 C		700 C	
	Nickel, a/o	Iron, a/o	Nickel, a/o	Iron, a/o
$UNi_2/(UNi_2 + X)$	56.9	9.8	56.7	10.0
$X/(UNi_2 + X)$	54.5	12.2	54.5	12.2
$X/(+ UFe_2)$	53.9	12.8	53.9	12.8
$UFe_2/(+ UFe_2)$	47.7	19.9	47.6	19.1

CRYSTALLOGRAPHY

The structure of UCo_2 and UNi_2 has been given by Baenziger [2], but for consistency, all the parameters here, including that of the X-phase are taken from Brooks [1].

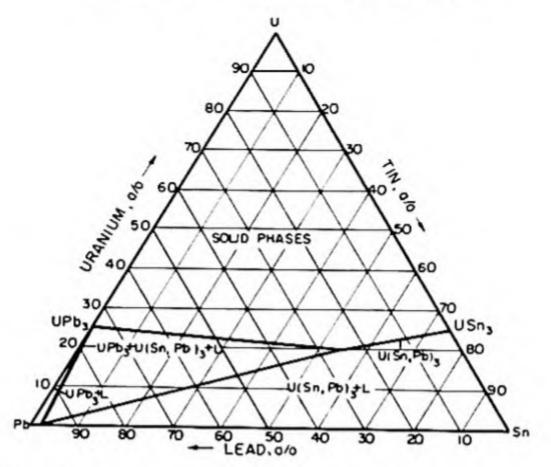| Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
UFe_2	Fcc	$a = 7.065$	8	12.5		Fd2m	C15 $MgCu_2$ structure
UNi_2	Hexagonal	$a = 4.959$ $c = 8.245$	4	13.5		$P6_3/mmc$	C14 $MgZn_2$ structure
X	Hexagonal	$a = 4.972$ $c = 16.425$	8			$P6_3/mmc$	C36 $MgNi_2$ structure

References

1. G. B. BROOKS, G. I. WILLIAMS and E. A. SMITH, "Pseudo-Binary Phase Sections Between Laves Phases in Ternary Alloys of Uranium," *J. Inst. Met.*, **83,** 271 (1954-55).

2. N. C. BAENZIGER, R. E. RUNDLE, A. I. SNOW and A. S. WILSON, "Compounds of Uranium With the First Long Period" (AECD 2598) *Acta Cryst.*, **3,** 34 (1950).

URANIUM-LEAD-TIN

THE CONSTITUTIONAL DIAGRAM

The portion of the uranium-lead-tin system at 350 C shown in the accompanying figure is from Teitel [1]. Extensive solubility of lead in USn_3 is indicated.

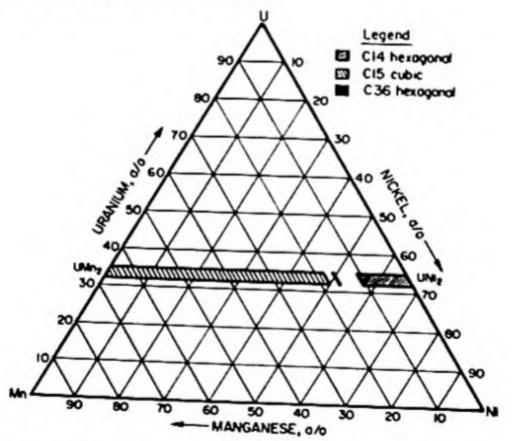The $U(Sn, Pb)_3$ phase exists in equilibrium with liquids containing up to 97.5 a/o lead.

CRYSTALLOGRAPHY

No new phases have been reported.

Reference

1. R. J. TEITEL, private communication (1956).

URANIUM-MANGANESE-NICKEL

THE CONSTITUTIONAL DIAGRAM

The pseudo binary UMn_2-UNi_2 has been studied [1]. The compound UMn_2 has the C15-type structure; the compound UNi_2 has the C14-type structure. Isotherms at 900 and 700 C show identical boundaries within

experimental error, and are given in the diagram. An intermediate phase,
X, with the C36-type structure was observed. In one alloy, an additional
pattern was observed; work with single crystals showed that the sample
had a hexagonal cell and an abnormally large spacing. This latter structure
could not be reproduced in other samples.

Solubility limits are given as:

	900 C		700 C	
	Nickel, a/o	Manganese, a/o	Nickel, a/o	Manganese, a/o
$UNi_2/(UNi_2 + X)$	55.9	10.7	55.9	10.7
$X/(UNi_2 + X)$	50.9	15.8	50.9	15.8
$X/(X + UMn_2)$	50.5	16.2	50.5	16.2
$UMn_2/(X + UMn_2)$	48.9	17.8	48.5	17.8

CRYSTALLOGRAPHY

The structure of UCo_2 and UNi_2 has been given by Baenziger [2], but
the parameters given here are all from Brooks [1], including those of the
intermediate phase, X.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
UMn_2	Fcc	$a = 7.156$	8	12.5		Fd3m	C15 MgCu₂ structure
UNi_2	Hexagonal	$a = 4.959$ $c = 8.245$	4	13.5		C6/mmc P6₃/mmc	C14 MgZn₂ structure
X	Hexagonal	$a = 4.986$ $c = 16.453$	8			P6₃/mmc	C36 MgNi₂ structure

References

1. G. B. BROOKS, G. I. WILLIAMS and E. A. SMITH, "Pseudo-Binary Phase Sections Between Laves Phases in Ternary Alloys of Uranium," *J. Inst. of Met.*, **83**, 271 (1954-55).
2. N. C. BAENZIGER, R. E. RUNDLE, A. I. SNOW and A. S. WILSON, "Compounds of Uranium With the First Long Period," (AECD 2598) *Acta Cryst.*, **3**, 34 (1950).

URANIUM-MOLYBDENUM-NIOBIUM

Data on the effect of molybdenum on the shape of the gamma-plus-gamma_2 loop which occurs in binary uranium-niobium alloys is available [1]. Metallographic and x-ray results indicate that 5 a/o molybdenum increases the extent of the loop to 50 to 57 a/o niobium at 1100 C, 30 to 65 a/o niobium at 850 C, and 15 to 69 a/o niobium at 800 C. The monotectoid temperature in an alloy containing 5 a/o molybdenum and 23 a/o niobium is 647 ± 5 C. No new phases have been observed at temperatures above 650 C.

CRYSTALLOGRAPHY

No new phases have been reported.

Reference

1. G. H. Bannister and J. R. Murray, United Kingdom, unpublished work, 1957.

URANIUM-MOLYBDENUM-RUTHENIUM

A study of the high-uranium portion of the system is reported [1]. The addition of about 5 a/o ruthenium to uranium-molybdenum alloys reduces molybdenum solubility in the gamma phase to approximately 23 a/o. At 660 C, the uranium-rich limit of the gamma phase occurs in an alloy containing about 4.5 a/o each of molybdenum and ruthenium. The gamma and beta-uranium phases exist in equilibrium with U_5Ru at this temperature.

CRYSTALLOGRAPHY
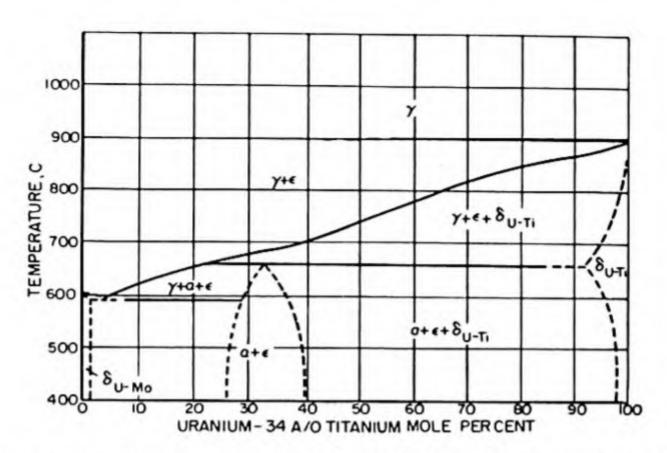
No new phases have been reported.

Reference

1. A. E. Dwight, "Nuclear Fuels Newsletter," WASH-702, May, 1957. Classified.

URANIUM-MOLYBDENUM-TITANIUM

THE CONSTITUTIONAL DIAGRAM

An investigation of the region between the delta phases of the uranium-molybdenum and uranium-titanium systems has been conducted on alloys ranging in composition from uranium-31.5 a/o molybdenum to uranium-34 a/o titanium [1]. The tentative ternary cut shown is based upon metallographic, x-ray, and thermal-analysis data.

In the compositional range investigated the three components show complete solubility at elevated temperatures. The epsilon phase which appears in these alloys is a body-centered cubic solid solution rich in molybdenum and titanium. With the formation of the uranium-titanium delta phase and with decreasing temperatures, the epsilon phase becomes depleted with respect to uranium; the gamma phase approaches the uranium-molybdenum eutectoid composition.

The absence of beta uranium in these alloys indicates that the equilibrium established between the gamma-uranium and uranium-titanium delta phases restricts the beta phase to high-uranium alloys. At lower temperatures, the equilibrium established between the alpha-uranium and epsilon phases restricts the delta-phase regions.

Ternary solubility of molybdenum and titanium in the respective delta phases is limited.
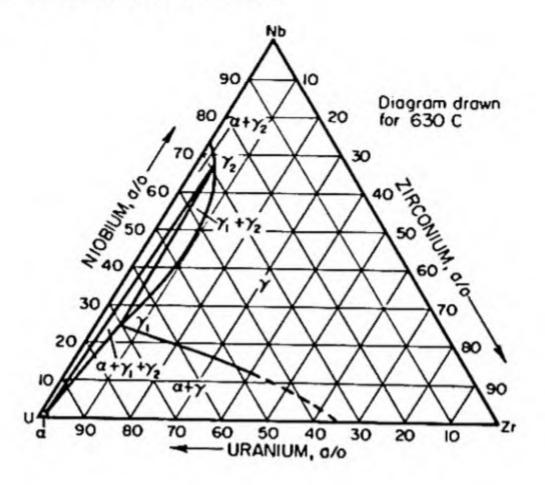
CRYSTALLOGRAPHY

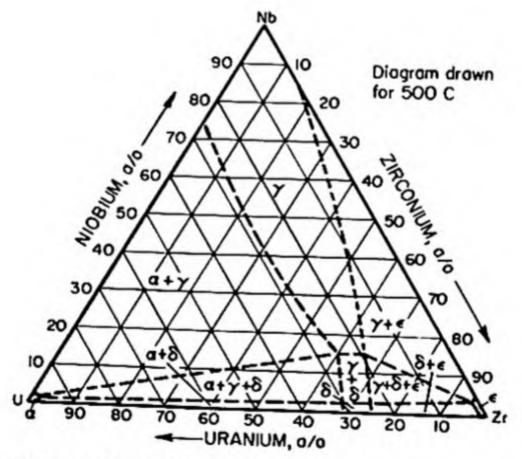No new phases have been reported.

Reference

1. H. A. SALLER, F. A. ROUGH, A. A. BAUER and J. R. DOIG, "Constitution of Delta-Phase Alloys of the System Uranium-Molybdenum-Titanium," BMI-1134 (September, 1956).

URANIUM-NIOBIUM-ZIRCONIUM

THE CONSTITUTIONAL DIAGRAM

The uranium-rich portion of the system has been investigated by Dwight and Mueller [1]. Ternary sections showing the phase boundaries as they exist at 630 and 500 C are shown in the accompanying figure.

At elevated temperatures, uranium, zirconium, and niobium exhibit complete solubility. The addition of about 2 a/o niobium closes the gamma$_1$-plus-gamma$_2$ loop in the uranium-zirconium system, while the

addition of 15 a/o zirconium is required to eliminate this loop in the uranium-niobium system. With the addition of 15 a/o niobium, the delta phase in the uranium-zirconium system is eliminated and the gamma phase is stabilized to room temperature.

CRYSTALLOGRAPHY

No new phases are reported.

Reference

1. A. E. DWIGHT and M. H. MUELLER, "Constitution of Uranium Niobium and Uranium-Niobium-Zirconium Systems," ANL-5581 (October, 1957).

URANIUM-OXYGEN-ZIRCONIUM

THE CONSTITUTIONAL DIAGRAM

The system was first investigated by Saller [1]. Confirmation of the phase relationships in the system has been reported by Rough [2] in the region of the intermediate delta phase of the uranium-zirconium system.

The delta phase is seen to be restricted in extent by oxygen additions. Solubility of oxygen in the uranium-zirconium delta phase is slightly less than 500 ppm, solubilities in the ternary section drawn for 540 C being exaggerated to permit illustration of the phase relationships.

The restriction of the delta phase is a consequence of the pronounced stabilizing effect of oxygen on the epsilon (alpha-zirconium) phase.[3] As a result of this stabilization, an equilibrium between the alpha-uranium and epsilon (alpha-zirconium) phases is set up which restricts the delta phase.

The same phase relationships exist for the gamma-uranium phase above the delta-phase transformation temperature. With increasing temperature the limits of the gamma phase in the binary system broaden until complete solubility exists as shown in the diagram drawn for a temperature of 1095 C.
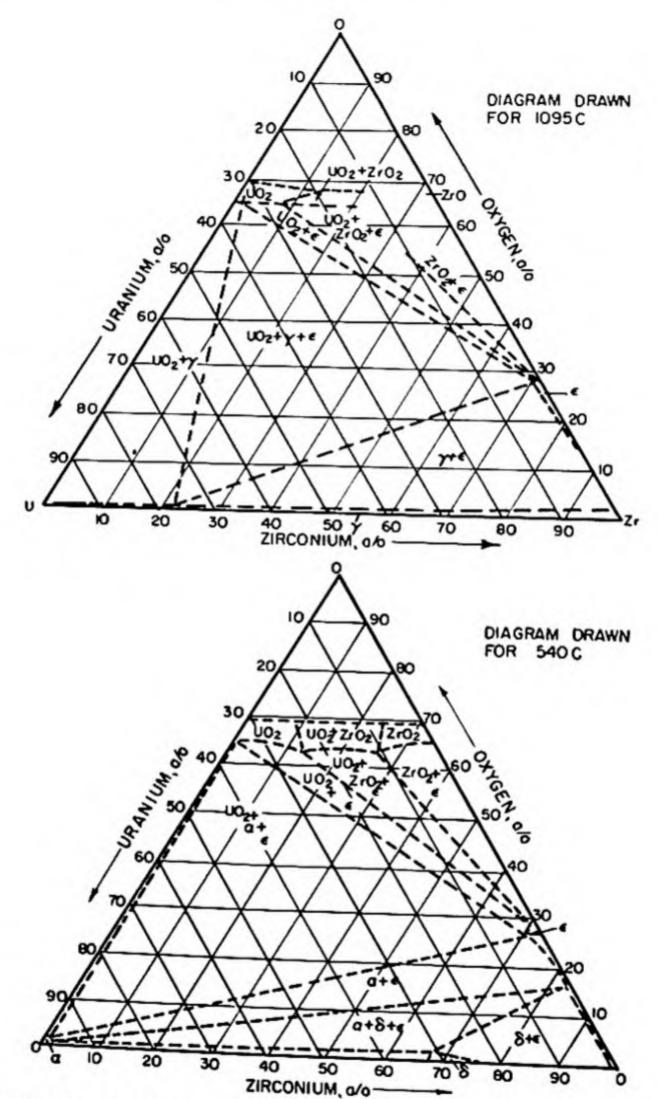
Solubility of oxygen in the gamma phase is limited.

CRYSTALLOGRAPHY

No new phases have been reported.

References

1. H. A. SALLER, F. A. ROUGH, A. A. BAUER and J. M. FACKELMANN, "Phase Relationships of the Uranium-Zirconium-Oxygen System Involving Zirconium and Uranium Dioxide," BMI-1023 (July 28, 1955).

DIAGRAM DRAWN
FOR 1095 C

DIAGRAM DRAWN
FOR 540 C

2. F. A. ROUGH, A. E. AUSTIN, A. A. BAUER and J. R. DOIG, "The Stability and Existence Range of the Zirconium-Uranium Epsilon Phase," BMI-1092 (May 28, 1956).

3. R. F. DOMAGALA and D. J. MCPHERSON, "Systems Zirconium-Oxygen," *Trans. AIME*, **200** (1954).

URANIUM-THORIUM-ZIRCONIUM

The effect of small additions of zirconium on the eutectic and liquid immiscibility gaps that occur in binary uranium-thorium alloys has been studied by thermal analysis and metallographic methods in arc-melted alloys.[1] No new phases were observed, the zirconium being dissolved in the thorium and uranium. With 13 a/o zirconium the pseudo binary eutectic occurs at 7 a/o thorium and 1168 C. No liquid immiscibility gap occurs in alloys containing 10 a/o zirconium.

CRYSTALLOGRAPHY

No new phases have been reported.

Reference

1. J. R. MURRAY, United Kingdom, unpublished information (1957).
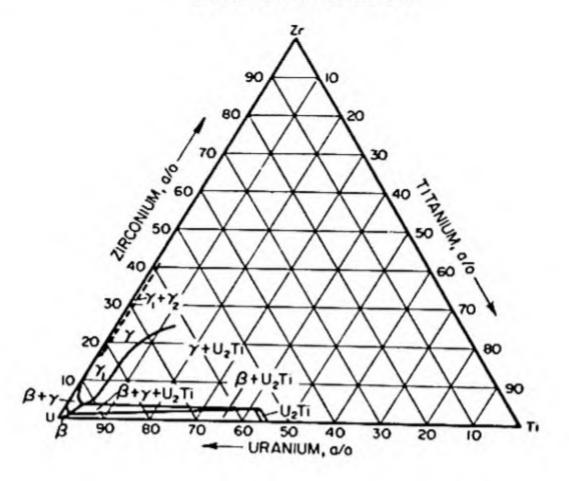
URANIUM-TITANIUM-ZIRCONIUM
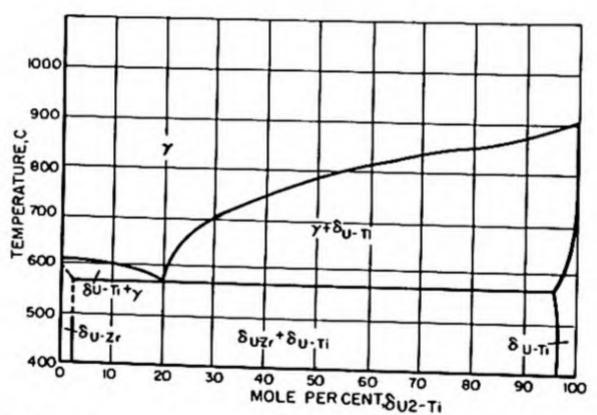
THE CONSTITUTIONAL DIAGRAM

An investigation of the region between the intermediate delta phases of the uranium-titanium and uranium-zirconium systems has been reported [1], as has been a study of the high-uranium portion of the system at temperatures of 700, 750, 800, and 850 C.[2] The results of both investigations are consistent with each other. A tentative ternary cut based upon data obtained from alloys ranging in composition from uranium-35 a/o titanium to uranium-74 a/o zirconium [1] is shown as is a ternary section for 700 C.[2]

At elevated temperatures uranium, titanium, and zirconium exhibit complete solid solubility. The gamma phase is stabilized to a temperature below the binary uranium-zirconium eutectoid.[1]

Ternary solubility of zirconium and titanium in the respective delta phases is limited.[1] Solubility of zirconium in U_2Ti decreases with increasing temperature; a corresponding decrease in extent of the gamma-plus-U_2Ti region accompanies this decreasing solubility.[2]

At 700 C the addition of less than 1.5 a/o titanium to uranium-zirconium alloys is responsible for the disappearance of the $gamma_1$-plus-$gamma_2$ field.[2]

CRYSTALLOGRAPHY

No new phases have been reported.

References

1. H. A. SALLER, F. A. ROUGH, A. A. BAUER and J. R. DOIG, "Constitution of Delta-Phase Alloys of the System Uranium-Zirconium-Titanium," *J. Metals*, 9, 878–81 (July, 1957).

2. B. W. HOWLETT, Associated Electrical Industries Research Laboratory, United Kingdom, unpublished information (1957).

MELTING POINTS AND ALLOTROPIC MODIFICATIONS OF THORIUM

The metal thorium is face-centered cubic at room temperature and body-centered cubic at high temperature.

The existence of a high-temperature thorium modification has been demonstrated by Chiotti [1], who employed high-temperature x-ray diffraction methods. Evidence for and confirmation of the allotropic change has been reported by a number of additional investigators [2-5].
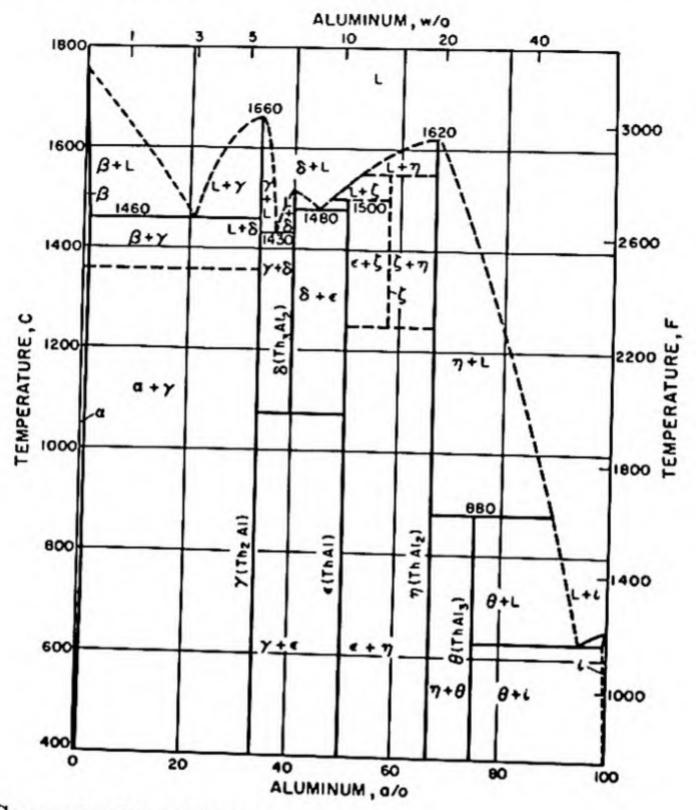
The temperature of the thorium transformation has been determined by Chiotti [6] to be 1360 ± 10 C and the melting point 1755 ± 10 C. These values were derived by studying thorium of varying carbon content and extrapolating the curves of transformation and melting temperatures back to zero carbon. These temperatures have been used to standardize the construction of the thorium constitutional diagrams.

The lattice constants of alpha and beta thorium vary somewhat with grade and degree of contamination. The lattice constants tabulated are for production-grade thorium. The lattice constant of alpha thorium increases from 5.089 A at room temperature to 5.161 A at 1200 C [1].

Phase	Unit cell			Density, g/cm^3		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Alpha	Fcc	$a = 5.089$			11.6		At room temperature
Beta	Bcc	$a = 4.12$					At 1400 C

References

1. P. Chiotti, "High-Temperature Crystal Structure of Thorium," *J. Electrochem. Soc.*, **101**, 567-70 (1954).

2. J. R. Murray, United Kingdom, unpublished information (June 25, 1952).

3. H. W. Deem, unpublished information (1953).

4. E. J. Boyle and R. E. Adams, unpublished information (1953).

5. W. B. Wilson, A. E. Austin and C. M. Schwartz, "The Solid Solubility of Uranium in Thorium and the Allotropic Transformation of Thorium-Uranium Alloys," BMI-1111 (July 12, 1956).

6. P. Chiotti, unpublished information (1955).

THORIUM-ALUMINUM

THE CONSTITUTIONAL DIAGRAM

The diagram shown is based on experiments by Murray [1], Braun and van Vucht [2, 3], and Leber [4]. There are six compounds in the system: Th_2Al, Th_3Al_2, $ThAl$, $ThAl_2$, $ThAl_3$, and a sixth compound stable only at high temperatures, with a composition between $ThAl$ and $ThAl_2$. There are many points of similarity between this diagram and an earlier one proposed by Saller and Rough [5] who obtained evidence for four intermetallic compounds.

Hansen [6] surveyed early experiments on these alloys. The result of this survey and the work of Grube and Botzenhardt [7] are in general agreement with the diagram as shown.

The solid solubility in aluminum in carefully homogenized alloys appears to be a maximum of 0.7–0.8 w/o thorium.[5] This estimate is based on

metallographic examination and thermal analyses of a series of alloys. Determinations of lattice constants indicate as much as 2.0 w/o thorium is soluble in aluminum.[7] The same report indicates that the solubility decreases with decreasing temperature. Another report indicates a solubility as low as 0.001 w/o thorium [8] on the basis of measurements on microhardness. This procedure appears to be questionable, at least in this case.

The solid solubility of aluminum in thorium is quite limited, being approximately 0.8 a/o aluminum at 1200 C.[1]

CRYSTALLOGRAPHY

The crystal structures of compounds in this system have been reported by Braun and van Vucht.[2, 3] Murray [9] has also reported the structures of Th_2Al, Th_3Al_2, $ThAl_2$, and $ThAl_3$, while Anderson and Goedkoop [10] confirmed the structure of $ThAl_2$ by neutron-diffraction studies. The $ThAl_3$ lattice parameters had been reported earlier by Brauer [11].

Some evidence for a high-temperature modification of the $ThAl_2$ phase has been reported by Saller and Rough [5].

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Gamma (Th_2Al)	Tetragonal	$a = 7.614$ $c = 5.857$	4	9.67	9.7	I4/mcm	Isomorphous with $CmAl_2$, Th_2Ag, Th_2Au, Th_2Cu, Th_2Zn
Delta (Th_3Al_2)	Tetragonal	$a = 8.125$ $c = 4.217$	2	9.0	9.0	P4/mbm	Isomorphous with U_3Si_2, Th_3Si_2
Epsilon ($ThAl$)	Orthorhombic	$a = 11.45$ $b = 4.42$ $c = 4.19$	4	8.11	8.10	C222	
Zeta (X)	Tetragonal	$a = 9.89$ $c = 7.81$					
Eta ($ThAl_2$)	Hexagonal	$a = 4.388$ $c = 4.162$	1	7.0	7.0	P6/mmm	Isomorphous with AlB_2, $ThCu_2$, $ThNi_2$, β-$ThSi_2$
Theta ($ThAl_3$)	Hexagonal	$a = 6.500$ $c = 4.626$	2	6.14	6.14	P6₃/mmc	Isomorphous with $SnNi_3$

References

1. J. R. MURRAY, United Kingdom, unpublished information (June, 1956).

2. P. B. BRAUN and J. H. N. VAN VUCHT, "Al-Th Intermetallic Compounds I," *Acta Cryst.*, **8**, 117 (1955).

3. P. B. BRAUN and J. H. N. VAN VUCHT, "Al-Th Intermetallic Compounds II," *Acta Cryst.*, **8**, 246 (1955).

4. A. LEBER, "On the System Al-Th," *Z. anorg. u. allgem. Chem.*, **166**, 16 (1927).

5. H. A. SALLER and F. A. ROUGH, private communication (1952).

6. M. HANSEN, *Der Aufbau der Zweistofflegierungen.* Edwards Bros. Inc., Ann Arbor, Michigan, 156 (1943).

7. G. GRUBE and L. BOTZENHARDT, "Alloys of Thorium With Copper, Aluminum, and Sodium," *z. Elektrochem.*, **48**, 422 (1942).

8. H. BUCKLE, "Solubility Determinations by Means of Micro-Hardness Tests," *Metallforschung*, **1**, 43 (1946).

9. J. R. MURRAY, "The Crystal Structures of Some Thorium Compounds," *J. Inst. Metals*, **4**, 91–96 (1955).

10. A. F. ANDERSEN and J. A. GOEDKOOP, "Neutron Diffraction Study of Al_2Th," *Acta Cryst.*, **8**, 118 (1955).

11. G. BRAUER, "Crystal Structure of Intermetallic Compounds of Aluminum With Titanium, Zirconium, Thorium, Columbium, and Tantalum," *Naturwissenschaften*, **26**, 710 (1938).

THORIUM-ANTIMONY

A diagram of the thorium-antimony system has not been worked out but there is evidence of three intermetallic compounds ThSb, Th_3Sb_4, and $ThSb_2$.[1] The solubility of thorium in liquid antimony has been reported [2] as:

Temperature, C	650	700	750	800	850	900
Solubility, w/o	<0.05	<0.05	0.1	0.3	0.5	1.0

CRYSTALLOGRAPHY

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
ThSb	Fcc	$a = 6.318$	4	9.32			NaCl-type structure, isomorphous with ThAs, ThC, ThN, USb
Th_3Sb_4	Bcc	$a = 9.374$	4	9.55		$I\bar{4}3d$	Isomorphous with Th_3P_4, Th_3As_4, Th_3Bi_4, U_3Sb_4
$ThSb_2$	Tetragonal	$a = 4.353$ $c = 9.172$	2	9.09		$P4/nmn$	Isomorphous with $ThAs_2$, $ThBi_2$, USb_2, Cu_2Sb

References

1. R. FERRO, "Crystal Structures of the Thorium Antimonides," *Acta Cryst.*, **9** (10), 817 (1956).

2. E. E. HAYES and P. GORDON, *J. Met. and Cer.*, TID-65, 130–41 (July, 1948). Classified.

THORIUM-ARSENIC

A diagram of the thorium-arsenic system has not been worked out but there is evidence of three intermetallic compounds, $ThAs$, Th_3As_4, and $ThAs_2$.

CRYSTALLOGRAPHY

The data below are from Ferro [1].

Phase	Unit cell			Density, g/cm^3		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
ThAs	Fcc	$a = 5.972$	4				NaCl-type structure, isomorphous with ThSb, ThC, ThN, UAs
Th$_3$As$_4$	Bcc	$a = 8.843$	4			I$\bar{4}$3d	Isomorphous with Th$_3$P$_4$, Th$_3$Sb$_4$, U$_3$As$_4$, Th$_3$Bi$_4$
ThAs$_2$	Tetragonal	$a = 4.086$ $c = 8.575$	2			P4/nmn	Isomorphous with ThSb$_2$, UAs$_2$, ThBi$_2$, Cu$_2$Sb

Reference

1. R. FERRO, "The Crystal Structures of the Thorium Arsenides," *Acta Cryst.*, **8**, 360 (1955).
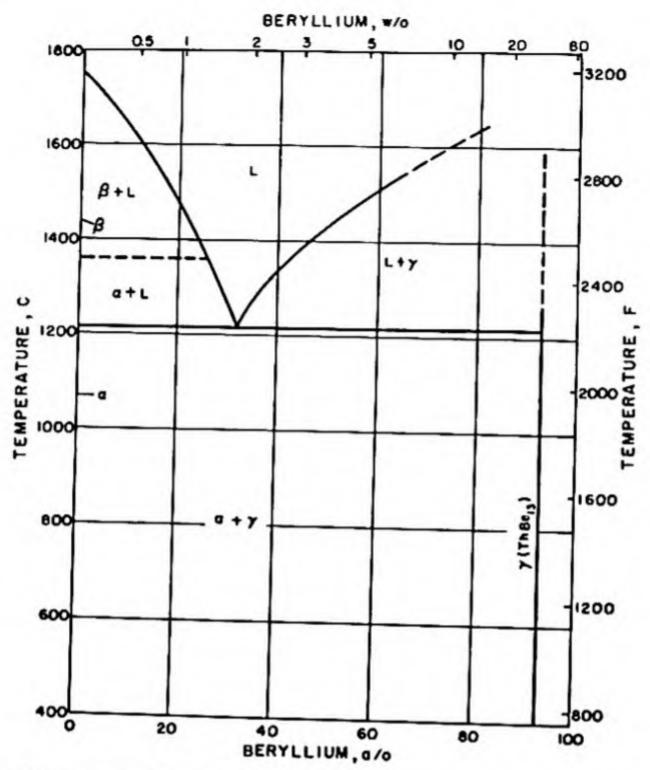

THORIUM-BERYLLIUM

THE CONSTITUTIONAL DIAGRAM

There is only one compound, $ThBe_{13}$, in this system. The portion of the system which is shown has been reported both by Spedding [1] and by Foote [2].

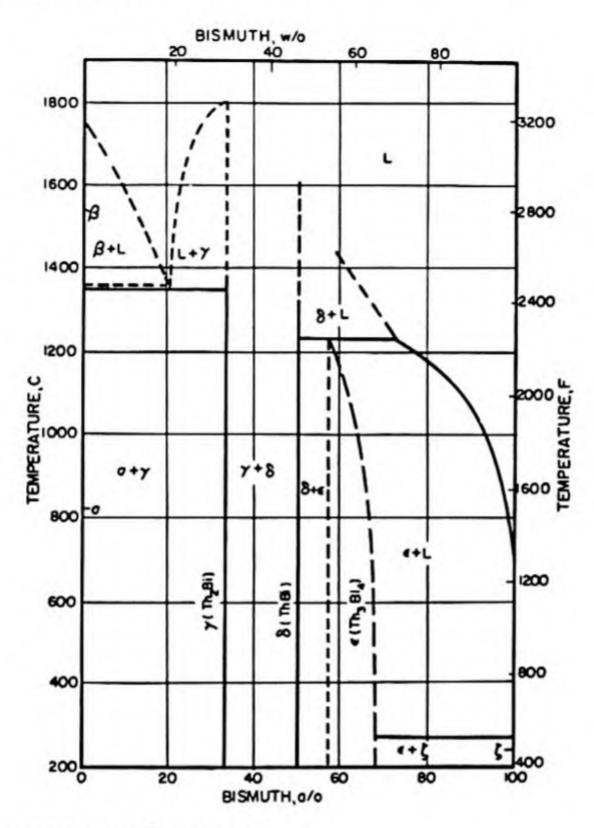The eutectic occurs at about 1.75 w/o beryllium and 1215 C.

CRYSTALLOGRAPHY

The compound $ThBe_{13}$ has been studied by Baenziger [3] and also by Koehler [4]. The data in the tabulation below are from Baenziger. Koehler confirms these data, on the basis of both x-ray and neutron-diffraction experiments.

| Phase | Unit cell | | | Density, g/cm³ | | Space group | Remarks |
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Gamma (ThBe₁₃)	Fcc	a = 10.395	8			Fm3C	Isomorphous with NaZn₁₃, ZrBe₁₃, CeBe₁₃, and UBe₁₃

References

1. F. H. SPEDDING, unpublished information (November, 1944).

2. FRANK FOOTE, Metallurgy Division Progress Report, CT-2794 (April, 1945).

3. N. C. BAENZIGER and R. E. RUNDLE, "The MBe13 Compounds" (AECD-2506), *Acta Cryst.*, 2, 258 (1945).

4. W. C. KOEHLER, J. SINGER and A. S. COFFINBERRY, "X-Ray and Neutron Diffraction Studies of the MBe13 Intermetallic Compounds," *Acta Cryst.*, 5, 394 (1952).

THORIUM-BISMUTH

THE CONSTITUTIONAL DIAGRAM

The diagram shown is from Bryner [1]; it is revised to include the compound Th_3Bi_4 as determined by Ferro [2]. Bryner had indicated this compound as having a composition corresponding to Th_3Bi_5. Earlier, Johnson [3] had reported the same compound as $ThBi_3$. Ferro has also identified $ThBi_2$ and reports that two phases close to ThBi in composition may exist.[2]

Alloys containing 20 to 100 w/o bismuth have also been investigated by Clinton [4]. His results, obtained by thermal analysis, are in substantial agreement with the diagram shown except that the liquidus is reported to rise more steeply, the liquidus of a 3 a/o thorium alloy being 1250 C.

A summary [5] of the solubility of thorium in bismuth as determined by several investigators [1, 6, 7] has been issued; the results show good agreement. Values as given by Hayes and Gordon [6] are:

Temperature, C	500	550	600	650	700	750	800	850	900
Solubility, w/o	0.1	0.2	0.3	0.5	0.7	1.1	1.5	2.3	3.2

Values for solubility obtained by Greenwood [8] show some scatter but tend to be slightly lower than those reported by other workers. He found that at low temperatures the solubility curve follows the relation

$$\log_{10} (\text{thorium, w/o}) = 3.02 - \frac{3220}{T}.$$

The following values were obtained:

Temperature, C	415	509	596	700	801	923	1042	1100
Solubility, w/o	0.04	0.08	0.39	0.43	1.25	2.2	4.2	5.6

CRYSTALLOGRAPHY

The data below are from Ferro [2].

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Th_3Bi_4	Bcc	$a = 9.559$	4	11.65		$I\bar{4}3d$	Isostructural with Th_3P_4, Th_3As_4, Th_3Sb_4, and U_3As_4
$ThBi_2$	Tetragonal	$a = 4.492$ $c = 9.298$	2	11.5		$P4/nmm$	Isostructural with $ThAs_2$, $ThSb_2$, UAs_2, and Cu_2Sb

References

1. J. S. BRYNER and R. J. TEITEL, private communication (1956).
2. R. FERRO, *Acta Cryst.*, **10**, 476 (1957).
3. H. B. JOHNSON, unpublished information (July, 1950).
4. D. M. CLINTON, United Kingdom, unpublished information (1955).
5. M. E. SIBERT, M. A. STEINBERG and R. J. TEITEL, *J. Electrochem Soc.*, **104**, 374 (1957).
6. E. E. HAYES and P. GORDON, *J. Met. and Cer.*, TID-65, BO-41 (July, 1948). Classified.
7. D. W. BAREIS, unpublished information (1957).
8. A. W. GREENWOOD, AERE M/R 2234 (1957).

THORIUM-BORON

Two borides, ThB_4 and ThB_6, have been observed and identified.

There is a eutectic between beta thorium and ThB_4 at about 1550 C. The melting point of ThB_4 is well above 2500 C.[1] The melting point of ThB_6 has been reported as 2195 C [2], but Brewer reports that ThB_6 is too unstable for refractory use.[1]

Boron has been reported to be soluble in thorium to some extent [3], but the amount has not been specified.

The lattice constant for ThB_4 did not vary in alloys containing 25 to 85 a/o boron; hence, it appears that ThB_4 has a very narrow solubility range.[1]

Existence of an additional boride at about 50 a/o boron has been reported.[3] This report probably should be discounted, since Brewer [1] has shown that thorium metal is present up to the composition of ThB_4. A third phase in this region, identified as a solid solution of ThO_2 and ThB_4 [1], may account for reports of additional borides.

CRYSTALLOGRAPHY

The tabulated data for ThB_4 are those of Zalkin and Templeton [4], while the data for ThB_6 are from the work of Kiessling [3].
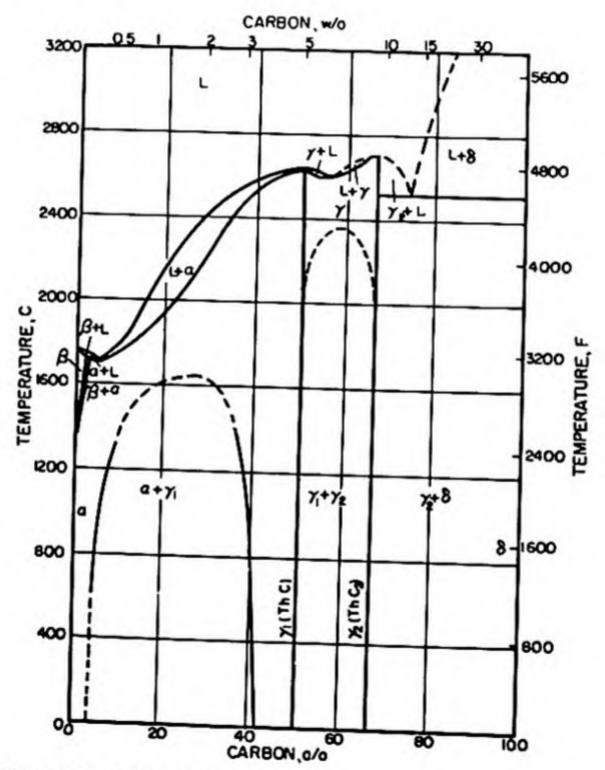
The hexaboride, ThB_6, was reported as early as 1932.[5, 6] More recent data are reported by Lafferty [2] and by Bertaut and Blum [7]. Lafferty gives the lattice constant for ThB_6 as $a = 4.15$ A. Bertaut [7] reports the same constant as $a = 4.1132$ A, and indicates that the alkali metals can replace thorium in the lattice, giving solid solutions described by $Th_XNa_{(1-X)}B_6$. Parameters are reported for these solutions for $1 - X = 0.44$ to 0.77.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
ThB_4	Tetrag-onal	$a = 7.256$ ± 0.004 $c = 4.113$ ± 0.002		8.45		P4/mbm	Isomorphous with CeB_4 and ThB_4
ThB_6	Cubic	$a = 4.16$					Isomorphous with hexaborides of Ba, Sr, Ca, Yb, La, Ce, Nd, Pr, Gd, Y, and Er

References

1. L. BREWER, D. L. SAWYER, D. H. TEMPLETON and C. H. DAUBEN, "The Borides of Uranium and Thorium," AECD-2823 (February 14, 1950).

2. T. M. LAFFERTY, "Boride Cathodes," *J. Appl. Phy.*, **22**, 299-309 (1951).

3. Roland Kiessling, "Borides of Some Transition Elements," *Acta Chem. Scand.*, **4**, 163 and 209–27 (1950).

4. Allan Zalkin and D. H. Templeton, "The Crystal Structure of CeB₄, ThB₄, and UB₄," *J. Chem. Phys.*, **18**, 391 (1950); *reprinted in Acta Cryst.*, **6**, 269–72 (March, 1953).

5. G. Allard, *Bull. soc. chim.* (France), **51**, 1213–15 (1932).

6. M. V. Stachelberg and F. Newmann, *Z. physik. Chem.*, (B) **19**, 314–20 (1932).

7. F. Bertaut and P. Blum, "Hexaborides and Alkaline Substitutions," *Compt. rend.*, **234**, 2631–33 (1952).

THORIUM-CARBON

THE CONSTITUTIONAL DIAGRAM

The diagram shown is from Chiotti [1]; it represents a tentative revision of his earlier work [2, 3]. The pronounced effect of carbon on the thorium transformation temperature and melting point is well established. In

fact, the values of 1360 and 1755 ± 10 C, respectively, were obtained by examining thorium of varying carbon content and extrapolating plots of the resultant data to zero carbon.

Reported values [1, 4, 5] of carbon solubility in alpha thorium vary with the experimental techniques employed in their determination and range from about 0.2 to 0.35 w/o carbon at room temperature. The solubility curve shown represents a workable interpretation until these discrepancies are resolved.
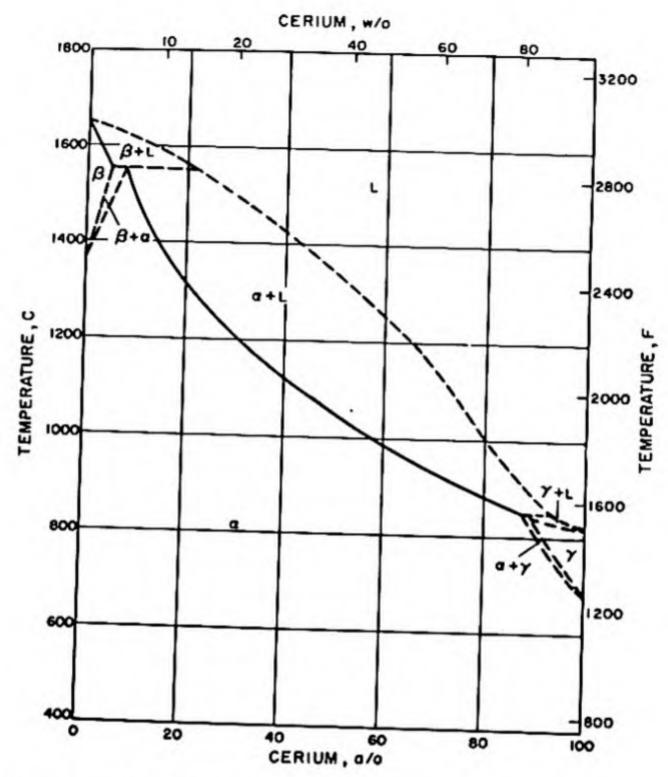
CRYSTALLOGRAPHY

The monocarbide, ThC, has the NaCl-type structure. The data in the table are from Chiotti [2, 3], who found that the lattice constant varied from 5.29 A at 3.9 w/o carbon to 5.34 A at 4.92 w/o carbon.

The dicarbide, ThC_2, was formerly believed to have a distorted-tetragonal structure [2]. Later studies by Hunt and Rundle [6], who used both x-ray and neutron-diffraction methods, have shown that it is c-centered monoclinic, as described in the tabulation. The positions of the thorium atom as determined by x-ray are the same in either space group, while satisfactory carbon positions have been found in C 2/c by neutron diffraction. Considerable covalent character is indicated for the Th-C bonds.[6]

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Gamma (ThC)	Fcc	a = 5.34	4				NaCl-type structure, isomorphous with ThN, UC, UN, and UO
Gamma (ThC₂)	c-Centered monoclinic	a = 6.53 b = 4.24 c = 6.56 β = 104°	4			C 2/c or Cc	

References

1. P. CHIOTTI, private communication (September, 1956).
2. P. CHIOTTI, "Thorium-Carbon System," AECD-3072 (June 5, 1950).
3. H. A. WILHELM and P. CHIOTTI, "Thorium-Carbon System," *Trans. Am. Soc. Metals*, **42**, 1295–1310 (1950).
4. D. PETERSON and R. MICKELSON, "Solubility of Carbon in Thorium," ISC-463 (February, 1954).
5. M. D. SMITH, United Kingdom, unpublished information (1954).
6. E. B. HUNT and R. E. RUNDLE, "The Structure of Thorium Carbide by X-ray and Neutron Diffraction" (AECD-3021), *J. Am. Chem. Soc.*, **73**, 4777–81 (1951).

THORIUM-CERIUM

CERIUM, w/o

THE CONSTITUTIONAL DIAGRAM

The diagram which is shown has been reported by Weiner [1]. All the alloys were prepared by arc melting. Lattice parameters of powders which had been annealed at 550 C showed a large negative deviation from Vegard's Law [1, 2].

Peterson [3] also investigated a series of thorium-cerium alloys and found that cerium and alpha thorium are completely soluble. He prepared the alloys by co-reduction at temperatures of 1000 to 1400 C. Earlier experiments by Foote [4] also indicated complete solubility in both the liquid and solid states in this system.
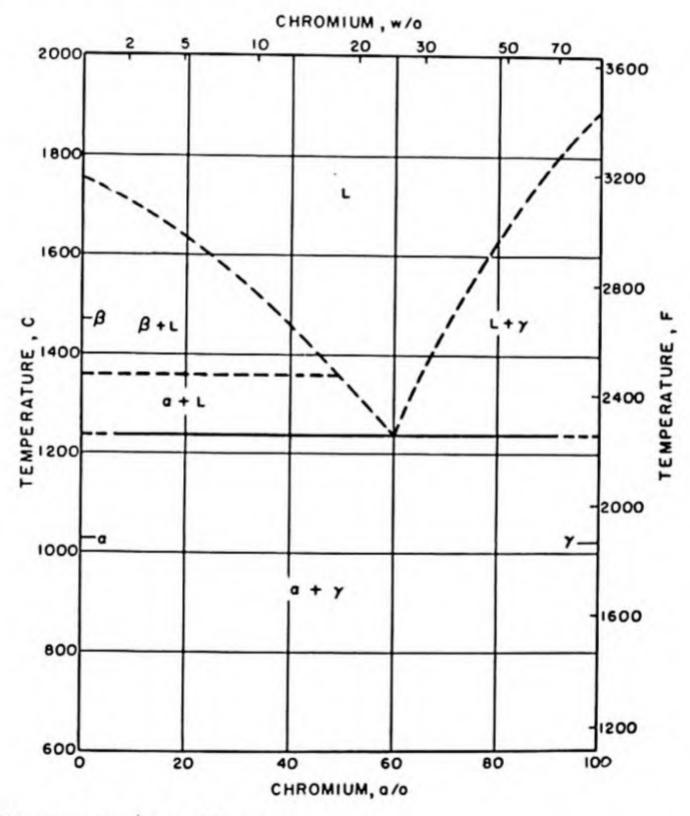
CRYSTALLOGRAPHY

No compounds occur in this system.

References

1. R. T. Weiner, United Kingdom, unpublished information (1956).
2. J. H. van Vucht, "Some Data About the System Cerium-Thorium,"
Philips Res. Rept., **12,** 351–54 (1957).
3. D. Peterson and R. Mickelson, unpublished information (March 31,
1952).
4. F. Foote, Division of Metallurgy Report, CT-2794 (April, 1945).

THORIUM-CHROMIUM

The Constitutional Diagram

The diagram which is shown has been reported by Wilhelm [1]. The
eutectic occurs at about 25 a/o chromium and 1235 C. The absence of
compounds in the system was confirmed by x-ray diffraction studies.

The solubility of thorium in chromium, and of chromium in thorium, is
quite limited.

CRYSTALLOGRAPHY

No compounds occur in this sytem.

Reference

1. H. A. WILHELM, A. S. NEWTON, A. H. DAANE and C. NEHER, "Thorium Metallurgy," CT-3714 (February, 1946).

THORIUM-COBALT

A diagram of the thorium-cobalt system has not been worked out, but there is evidence of five intermetallic compounds, Th_7Co_3, $ThCo$, $ThCo_{2-3}$, $ThCo_5$, and Th_2Co_{17}.

CRYSTALLOGRAPHY
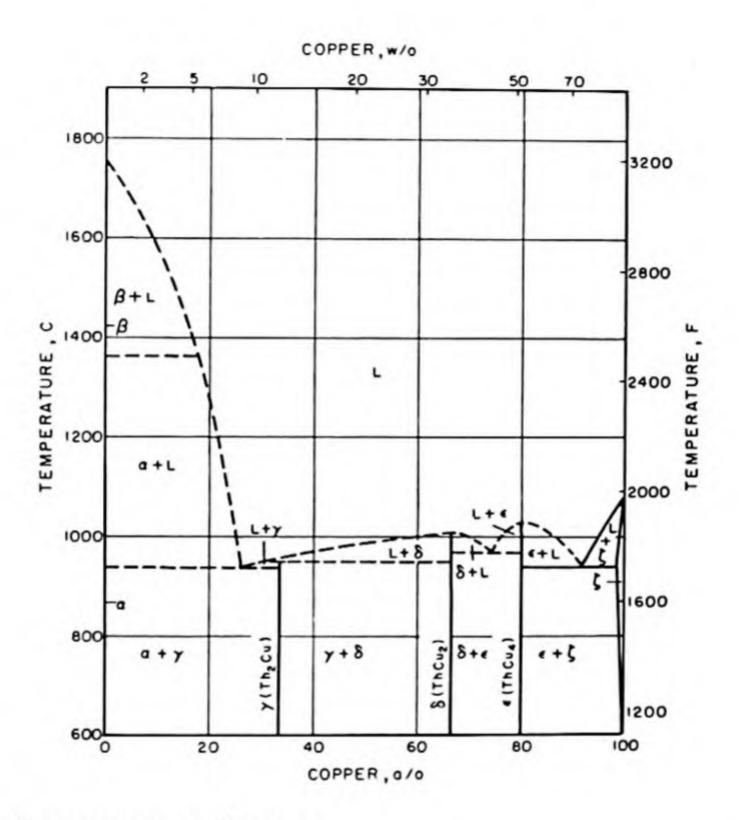
The data below are from Florio, Baenziger, and Rundle [1].

Florio, Baenziger, and Rundle [1] report that Th_2Co_{17}, Th_2Fe_{17}, Th_2Ni_{17}, and $ThMn_{12}$ are all related, even though different crystal classes are represented. The structures appear to be based on the $MgZn_5$ lattice in which thorium replaces magnesium and the transition element replaces zinc. It is reported that the superlattices of hexagonal Th_2Ni_{17}, monoclinic Th_2Fe_{17} and Th_2Co_{17}, and body-centered tetragonal $ThMn_{12}$ can be derived by systematic replacement of particular thorium atoms in the $MgZn_5$ lattice with pairs of transition-element atoms.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Th_7Co_3	Hexagonal	$a = 9.83$ $c = 6.17$	2			C6mc	Isomorphous with Th_7Fe_3 and Th_7Ni_3
$ThCo$	Orthorhombic	$a = 3.74$ $b = 10.88$ $c = 4.16$	4			Cmcm or Cmc	
$ThCo_{2-3}$	Hexagonal	$a = 5.03$ $c = 24.54$				C6/mmc, C6mc, or C$\bar{6}$2c	True c dimension is 8 or 9 times the c_a or about 200 A
$ThCo_5$	Hexagonal	$a = 5.01$ $c = 3.97$	1			C6/mmm	Isomorphous with $CaZn_5$, $ThFe_5$, and $ThNi_5$
Th_2Co_{17}	Monoclinic	$a = 9.62$ $b = 8.46$ $c = 6.32$ $\beta = 99°6'$	2			C2/m	Isomorphous with Th_2Fe_{17}

Reference

1. J. V. FLORIO, N. C. BAENZIGER and R. E. RUNDLE, "Compounds of Thorium With Transition Metals II. Systems With Iron, Cobalt, and Nickel," *Acta Cryst.*, **9**, 367–72 (1956).

THORIUM-COPPER

THE CONSTITUTIONAL DIAGRAM

The thorium-copper diagram which is shown is based on data of Wilhelm [1], Snow and Rundle [2], Grube and Botzenhardt [3], and Murray [4]. There appear to be three compounds in the system: Th_2Cu, $ThCu_2$, and $ThCu_4$.

Raube and Engel [5], who have a different view of the nature of the system, report four compounds, nominally Th_3Cu_5, $ThCu_3$, $ThCu_5$, and $ThCu_6$.

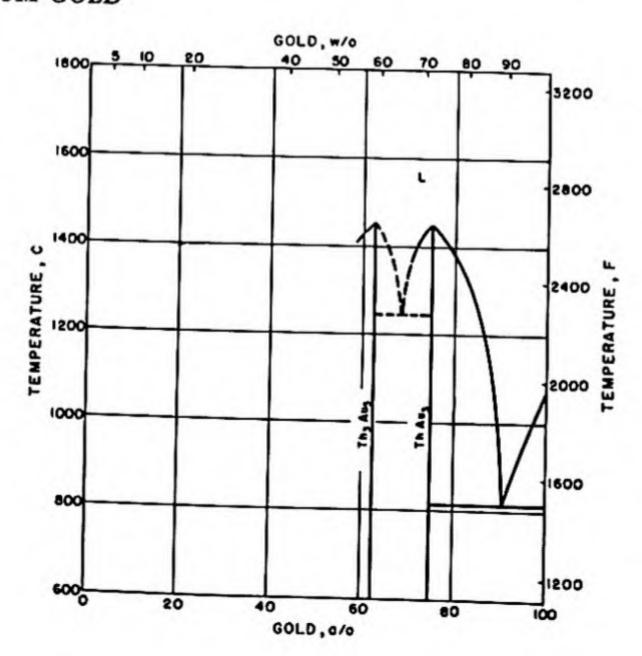The compounds in this system are pyrophoric [5].

CRYSTALLOGRAPHY

The tabulated data are from Snow and Rundle [2].

Phase	Unit cell			Density, g cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Gamma (Th₂Cu)	Bc tetragonal	$a = 7.29$ $c = 5.75$	4				C16-type structure, isomorphous with CuAl₂
Delta (ThCu₂)	Hexagonal	$a = 4.36$ $c = 3.48$	1			P6/mmm	C32-type structure, isomorphous with AlB₂
Epsilon (ThCu₄)	Not available						

References

1. H. A. WILHELM, A. S. NEWTON, A. H. DAANE and C. NEHER, "Thorium Metallurgy," CT-3714 (February, 1946).

2. A. I. SNOW and R. E. RUNDLE, unpublished information (July and November, 1949).

3. G. GRUBE and L. BOTZENHARDT, *Z. Elektrochem.*, **48**, 422 (1942).

4. J. R. MURRAY, "The Crystal Structure of Some Thorium Compounds," *J. Inst. Metals*, **4**, 91–6 (1955).

5. E. RAUB and M. ENGEL. *Z. Elektrochem.*, **49**, 487–93 (1943).

THORIUM-GOLD

THE CONSTITUTIONAL DIAGRAM

The portion of the diagram shown is from Raub and Engel [1]. The crystal structure of an additional pyrophoric compound, Th_2Au, has been reported by Murray [2].

The solubility in gold is less than 0.5 w/o thorium.[1]

The compounds shown in the diagram tend to be pyrophoric.[3]

CRYSTALLOGRAPHY

The data below for Th_2Au are from Murray [2].

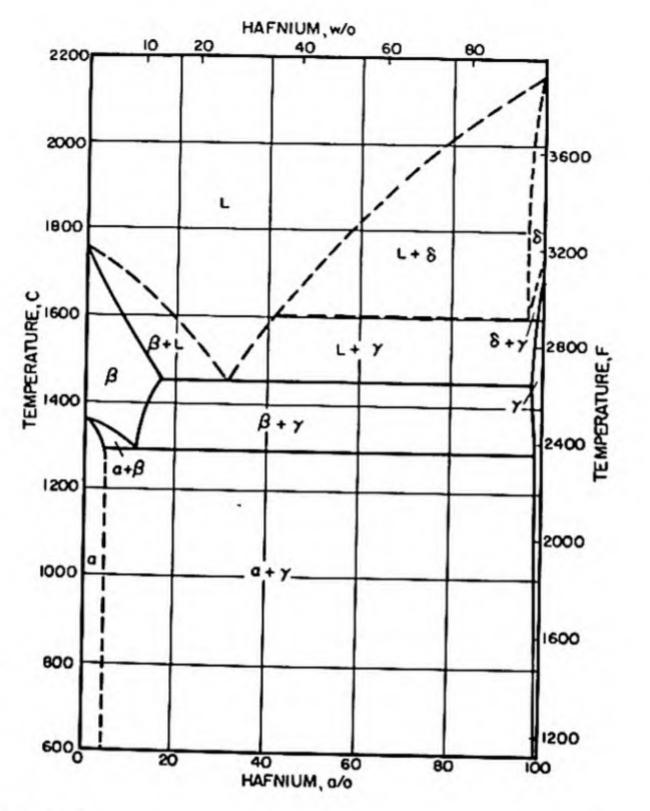| Phase	Unit cell			Density, g/cm^3		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Th_2Au	Tetragonal	a = 7.42 c = 5.95	4			I4/mcm	Isomorphous with $CuAl_2$, Th_2Al, and Th_2Ag

References

1. E. RAUB and M. ENGEL, "Alloys of Thorium With Copper, Silver, and Gold," *Z. Electrochem.*, **49**, 487–93 (1943).

2. J. R. MURRAY, "The Crystal Structure of Some Thorium Compounds," *J. Inst. Metals*, **4**, 91–6 (1955).

3. E. RAUB and M. ENGEL, "Self-Igniting Alloys," *Metallforschung*, **2**, 115–19 (1947).

THORIUM-HAFNIUM

THE CONSTITUTIONAL DIAGRAM

The diagram shown is from Loomis and Carlson [1]. A variety of techniques were employed in the determination.

Solubility of hafnium in beta thorium is approximately 17 a/o at the eutectic temperature. Solubility in the terminal alpha, gamma, and delta phases is limited.

CRYSTALLOGRAPHY

There are no intermetallic compounds in the system thorium-hafnium.

Reference

1. B. A. LOOMIS and O. N. CARLSON, "Thorium and Hafnium Phase Diagram," ISC-766 (1956); *Trans. Am. Soc. Metals*, **50** (1958).

THORIUM-HYDROGEN

Two hydrides have been identified: ThH_2 [1] and Th_4H_{15} [2].

A study of dissociation pressures in the thorium-ThH_2 range has revealed a solubility in thorium of about 13 a/o hydrogen at 650 C and about 23 a/o hydrogen at 900 C.[3]

The solubility range of the dihydride, ThH_2, appears to be limited.[1]

CRYSTALLOGRAPHY

The crystallography of the hydrides ThH_2 and Th_4H_{15} is summarized in the tabulation below.

Rundle, Schull, and Wollan [1] have studied ThH_2 and ThD_2 and have determined the lattice constants and thorium-atom positions by x-ray diffraction, the hydrogen-atom positions by neutron diffraction.

The structure of ThH_2 is tetragonal, and there appears no likelihood that it will prove to be monoclinic, as did the "pseudo-tetragonal" ThC_2. The structure is of the distorted-fluorite type.[1]

The data for Th_4H_{15} are from Zachariasen [2].

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
ThH_2	Bc tetragonal	$a = 4.10$ ± 0.03 $c = 5.03$ ± 0.03	2	9.20			Isomorphous with ZrH_2
Th_4H_{15}	Cubic	$a = 9.11$ ± 0.02	4			I$\bar{4}$3d	

References

1. R. E. RUNDLE, C. G. SCHULL and E. O. WOLLAN, "The Crystal Structure of Thorium and Zirconium Dihydrides by X-ray and Neutron Diffraction," *Acta Cryst.*, **5**, 22–26 (1952).

2. W. H. ZACHARIASEN, "Crystal Chemical Studies of the 5f-Series of Elements XIX. The Crystal Structure of the Higher Thorium Hydride," *Acta Cryst.*, **6**, 393–95 (1953).

3. M. W. MALLETT and IVOR CAMPBELL, "The Dissociation Pressures of the Dihydride in the Thorium-Thorium Dihydride System," *J. Am. Chem. Soc.*, **73**, 4850–52 (1951).

THORIUM-INDIUM

The solubility of thorium in liquid indium is reported to be undetectable at 650 C and to be 0.25 and 0.95 w/o at 800 and 900 C, respectively.

CRYSTALLOGRAPHY

No data are available.

Reference

1. E. E. HAYES and P. GORDON, *J. Met. and Cer.*, TID-65, 130–41 (July, 1948).

THORIUM-IRIDIUM

A compound, $ThIr_2$, has been identified.[1] No other data are available.

CRYSTALLOGRAPHY

Data for $ThIr_2$ [1] are given below.

Phase	Unit cell			Density, g/cm^3		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
$ThIr_2$	Cubic	$a = 7.6615$	8			Fd3m	MgCu$_2$-type structure

Reference

1. A. E. DWIGHT, J. M. DOWNEY and R. A. CONNER, JR., "The Laves Phases $ThOs_2$ and $ThIr_2$," submitted to *J. Metals* (October 7, 1957).

THORIUM-IRON

There are four intermetallic compounds in the thorium-iron system: Th_7Fe_3, $ThFe_3$, $ThFe_5$, and Th_2Fe_{17} [1].

The compound Th_7Fe_3 appears to form by peritectic reaction between 850 and 1000 C.[2] A eutectic has been reported at 46 a/o iron and 860 C.[3] This composition is between Th_7Fe_3 and the next compound, $ThFe_3$.

There is evidence of some solubility of iron in thorium [2] and of thorium in iron [4], but the regions of both solid solutions are limited.

CRYSTALLOGRAPHY

The data given in the tabulation below are from Florio, Baenziger, and Rundle [1].

It is reported [1] that Th_2Fe_{17}, Th_2Co_{17}, Th_2Ni_{17}, and $ThMn_{12}$ are all related even though different crystal classes are represented. The structures appear to be based on the $MgZn_5$ lattice in which thorium replaces magnesium and the transition element replaces zinc. It is proposed that by systematic replacement of particular thorium atoms in the $MgZn_5$ lattice with pairs of transition element atoms, the superlattices of hexagonal Th_2Ni_{17}, monoclinic Th_2Fe_{17}, and Th_2Co_{17}, and body-centered tetragonal $ThMn_{12}$ can be derived.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, Å	Number of molecules	X-ray	Other		
Th_7Fe_3	Hexagonal	$a = 9.85$ $c = 6.15$	2			C6mc	Isomorphous with Th_7Co_3 and Th_7Ni_3
$ThFe_3$	Hexagonal	$a = 5.22$ $c = 24.96$	9			$C\bar{6}m_2$	
$ThFe_5$	Hexagonal	$a = 5.13$ $c = 4.02$	1			C6/mmm	Isomorphous with $CaZn_5$, $ThCo_5$, and $ThNi_5$
Th_2Fe_{17}	Monoclinic	$a = 9.68$ $b = 8.56$ $c = 6.46$ $\beta = 99°20'$	2			C2/m	Isomorphous with Th_2Co_{17}

References

1. J. V. FLORIO, N. C. BAENZIGER and R. E. RUNDLE, "Compounds of Thorium With Transition Metals II. Systems With Iron, Cobalt, and Nickel," *Acta Cryst.*, **9**, 367–72 (1956).

2. F. FOOTE, unpublished information (March, 1945).

3. H. A. WILHELM, A. S. NEWTON, A. H. DAANE and C. NEHER, "Thorium Metallurgy," CT-3714 (February, 1956).

4. H. W. RUSSELL, unpublished information (August, 1946).

THORIUM-LANTHANUM

Peterson [1] studied a series of thorium-lanthanum alloys metallographically and found that lanthanum and thorium exhibit extensive solubility. The alloys were prepared by co-reduction at 1000 to 1400 C.
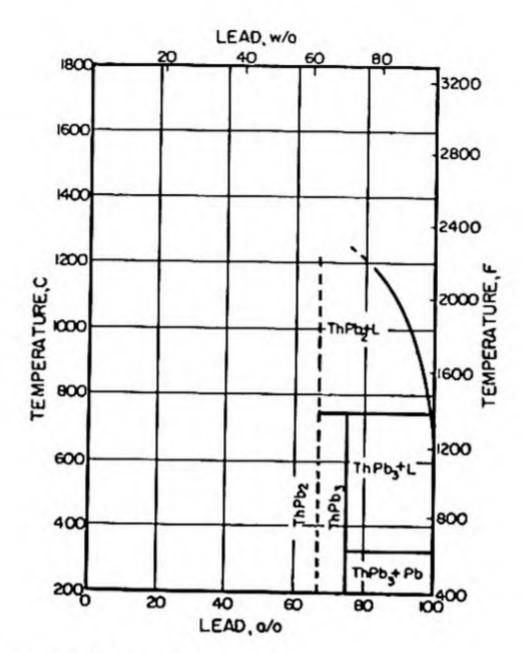
CRYSTALLOGRAPHY

There are no compounds in this system.

Reference

1. D. PETERSON and R. MICKELSON, unpublished information (March 31, 1952).

THORIUM-LEAD

THE CONSTITUTIONAL DIAGRAM

A portion of the diagram has been determined by Bryner [1]. The compound $ThPb_2$ may show a limited solubility range. Weiner [2] has also investigated this system and reported the existence of two pyrophoric compounds $ThPb$ and $ThPb_3$. Metallographic examination showed that the solubility of lead in thorium was less than 1 a/o at 625 C.[2]
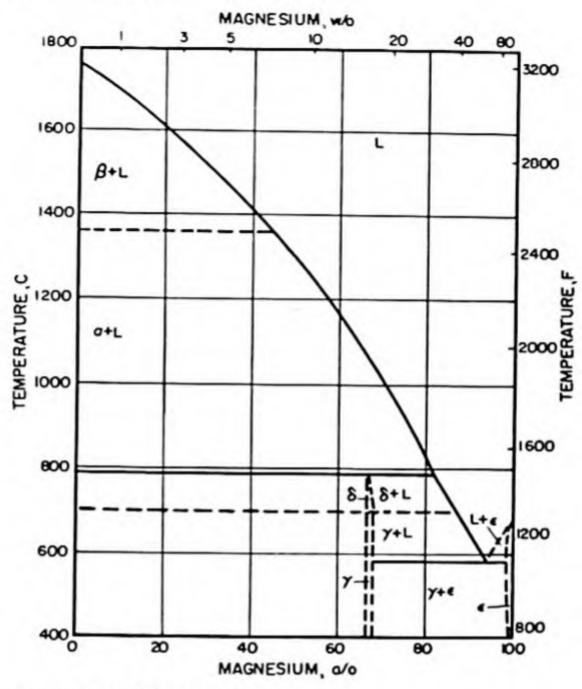
The compound $ThPb_3$ has a density of 12.3 g/cm^3.[1]

CRYSTALLOGRAPHY

No data are available on the crystal structure of the compounds.

References

1. J. S. BRYNER and R. J. TEITEL, private communication (1956).
2. R. T. WEINER, United Kingdom, unpublished information (1956).

THORIUM-MAGNESIUM

THE CONSTITUTIONAL DIAGRAM

The diagram shown is from Peterson [1, 2]. He reports a single compound, $ThMg_2$, which transforms from hexagonal to cubic symmetry at about 700 C. The cubic phase decomposes peritectically at about 790 C. The composition of the compound was determined by chemical analysis of crystals of the compound mechanically separated from the matrix of thorium-magnesium alloys.

This $ThMg_2$ phase reported by Peterson apparently corresponds to the cubic $ThMg_5$ phase reported by Yamamota, Levinson, and Rostoker [3], who report an additional unidentified compound of higher thorium composition. The composition $ThMg_5$ was determined by means of quantitative metallography.

The eutectic composition is reported (3) to be approximately 8 a/o thorium with maximum solubility of thorium in magnesium, 0.5 a/o, occurring at the eutectic temperature. The solubility decreases to 0.1 a/o at 300 C.[3]

The solubility of magnesium in thorium appears to be low [1], since no change in the thorium lattice constant was observed in thorium-magnesium alloys at room temperature.

CRYSTALLOGRAPHY

The data tabulated below are from Peterson [1]. The delta $ThMg_2$ phase is stable above about 700 C; the cubic gamma $ThMg_2$ is stable below this temperature.

| Phase | Unit cell | | | Density, g cm^3 | | Space group | Remarks |
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Gamma ($ThMg_2$)	Hexagonal	$a = 6.086$ $c = 19.64$				P6$_3$/mmc	Isomorphous with Ni_2Mg
Delta ($ThMg_2$)	Cubic	$a = 8.570$	8			Fd3m	Isomorphous with Cu_2Mg

References

1. D. PETERSON, unpublished information (March, 1954).
2. D. R. PETERSON, P. F. DILJAK and C. L. VOLD, "The Structure of Thorium-Magnesium Intermetallic Compounds," *Acta Cryst.*, 1-90, 1036 (1956).
3. A. S. YAMAMOTO, D. W. LEVINSON and W. ROSTOKER, "Research on Phase Relationships in Magnesium Alloys," WADC TN-649 (November 1, 1955).

THORIUM-MANGANESE

There is evidence of three intermetallic compounds: $ThMn_2$, Th_6Mn_{23}, and $ThMn_{12}$.[1]

Wilhelm [2] reports that a eutectic occurs at 911 C at a composition greater than 20 a/o manganese. Addition of 1 a/o manganese lowers the thorium lattice constant to $a = 5.0746$ A.[2]

CRYSTALLOGRAPHY

The data tabulated below are from Florio, Rundle, and Snow [1].

There is a similarity in the structures of Th_6Mn_{23} and $ThMn_{12}$ [1]. In both structures, body-centered cubes of manganese atoms tie thorium atoms together. In the Th_6Mn_{23} structure, each such cube has a thorium atom attached to each face, while in $ThMn_{12}$ only two opposite faces are bound to thorium.

Florio, Baenziger, and Rundle [3] report that $ThMn_{12}$, Th_2Fe_{17}, Th_2Co_{17}, and Th_2Ni_{17} are all related, and, while they represent different classes of crystals, appear to be based on the $MgZn_5$ lattice. A more complete discussion of their relationship is presented in "The System Thorium-Iron."

Phase	Unit cell			Density, g cm^3		Space group	Remarks
	Type	Dimensions A	Number of molecules	X-ray	Other		
ThMn$_2$	Hexagonal	$a = 5.48$ ± 0.01 $c = 8.95$ ± 0.02				P6$_3$ mmc	C14-type structure, isomorphous with MgZn$_2$
Th$_6$Mn$_{23}$	Fcc	$a = 12.523$ ± 0.001	4	9.03	9.02 ± 0.05	Fm3m	Density for 81.8 a/o manganese alloy
ThMn$_{12}$	Tetragonal	$a = 8.74$ ± 0.01 $c = 4.95$ ± 0.01	2		8.12	I4 mmm	

References

1. J. V. FLORIO, R. E. RUNDLE and A. I. SNOW, "Compounds of Thorium With Transition Metals" (AECD-3249), *Acta Cryst.*, **5**, 449–57 (1952).

2. H. A. WILHELM, A. S. NEWTON, A. H. DAANE and C. NEHER, "Thorium Metallurgy," CT-3714 (February, 1946).

3. J. V. FLORIO, N. C. BAENZIGER and R. E. RUNDLE, "Compounds of Thorium With Transition Metals: II. Systems With Iron, Cobalt, and Nickel," *Acta Cryst.*, **9**, 367–72 (1956).

THORIUM-MERCURY

THE CONSTITUTIONAL DIAGRAM

The diagram shown is from Domagala [1]. Data were obtained by employing a closed system. The alloy specimens, which were enclosed in small capsules, attained equilibrium with the vapor pressure of mercury as dictated by pressure and composition.
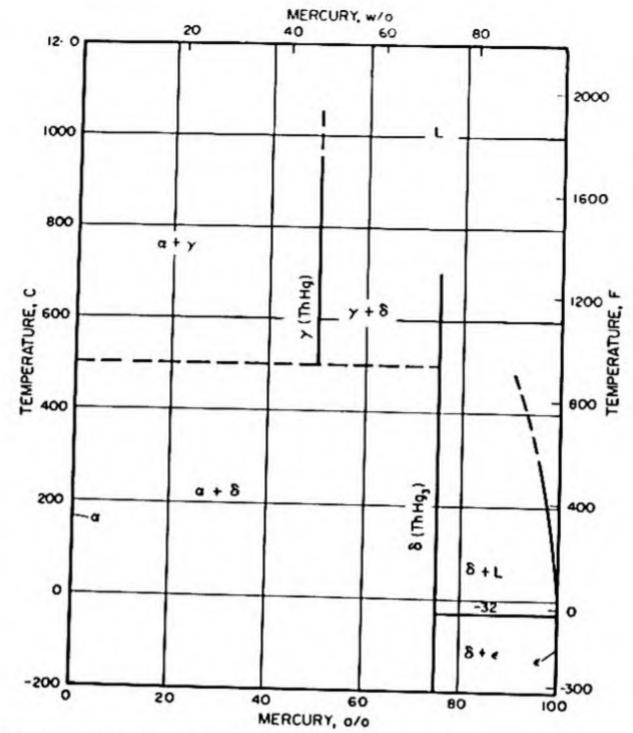
Two compounds appear in the system, ThHg and ThHg$_3$. The ThHg decomposes eutectoidally at some temperature between 400 and 600 C.[1]

Solubility of thorium in liquid mercury is given as 5 w/o at 300 C.[1] The solubility at 25 C has been reported as 0.154 w/o thorium.[2]

The solubility of mercury in solid thorium appears negligible.

CRYSTALLOGRAPHY

The data tabulated for ThHg$_3$ are from Domagala [1] and Baenziger [3]. Baenziger gives cell dimensions of $a = 3.38$ A and $c = 4.92$ A, rather than the values given which are from Domagala. Domagala reports that ThHg$_3$ exhibits a disordered structure with only two atoms per unit cell. In contradiction to the work of Baenziger, Domagala reports a very

restricted homogeneity range for ThHg₃ since alloys on either side of the phase showed identical lattice parameters.

Data for ThHg are from Domagala [1]. Weak superlattice lines were exhibited by this phase.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Gamma (ThHg)	Fcc	$a = 4.80$					
Delta (ThHg₃)	Hexagonal	$a = 3.361$ $c = 4.905$	$\frac{1}{2}$	14.2			Appears isomorphous with UHg₃

References

1. R. F. Domagala, R. P. Elliott and W. Rostoker, "The System Mercury-Thorium," to be published, *J. Metals* (1958).
2. W. G. Park and G. E. Prime, *J. Am. Chem. Soc.*, **58**, 1413 (1936).
3. N. C. Baenziger, R. E. Rundle and A. I. Snow, *Acta Cryst.*, **9**, 93 (1956).

THORIUM-MOLYBDENUM

Metallographic examination of high-molybdenum alloys showed that thorium was present as a second phase. Hence, no intermetallic compounds occur in this system.[1, 2] A eutectic is reported to occur at 38 a/o (20 w/o) molybdenum and 1380 C.[3]
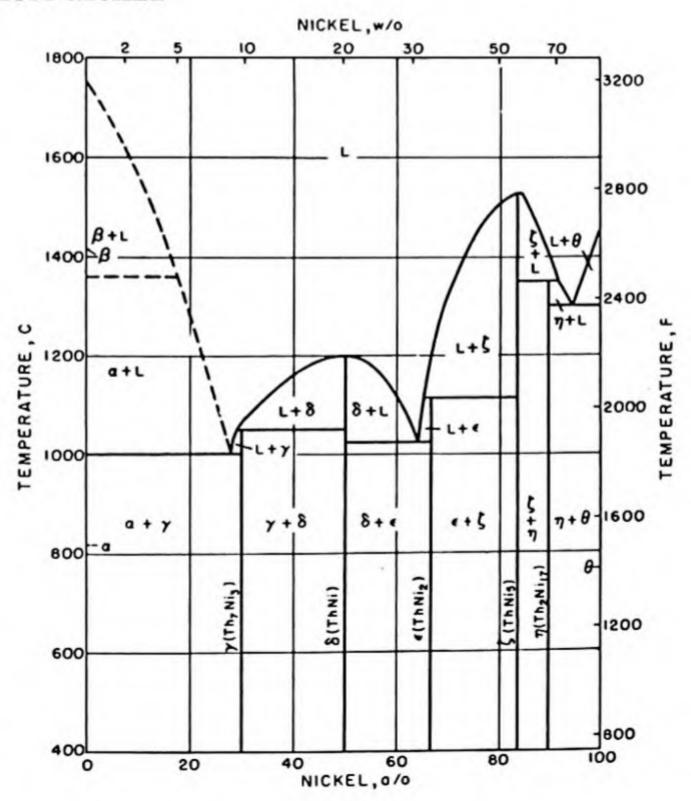
CRYSTALLOGRAPHY

No compounds occur in this system.

References

1. F. A. ROUGH, private communication (1952).
2. E. PIPITZ and R. KIEFFER, Z. Metallkunde, **46,** 187–94 (1955).
3. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.

THORIUM-NICKEL

THE CONSTITUTIONAL DIAGRAM

The diagram which is shown is that of Horn and Wasserman [1]; it has been revised to incorporate changes indicated by the work of Wilhelm and Carlson [2].

The melting points of compounds reported by Wilhelm and Carlson agree fairly well with similar data of Horn and Wasserman. The compounds in the system are Th_7Ni_3, $ThNi$, $ThNi_2$, $ThNi_5$, and Th_2Ni_{17}. [2, 3, 4] Horn and Wasserman [1] have reported the compounds tentatively as Th_2Ni, $ThNi$, Th_2Ni_5, $ThNi_5$, and $ThNi_9$, but this determination was not based on x-ray examination.

Carlson [2] has shown that the lattice constant for nickel is affected little by addition of 4 a/o thorium. Accordingly, the solubility of thorium in nickel is slight.

CRYSTALLOGRAPHY

The data tabulated are from Florio, Baenziger, and Rundle [3].

There was evidence of a range of composition in $ThNi_5$ to perhaps $ThNi_4$ [3].

It is reported [3] that Th_2Ni_{17}, Th_2Fe_{17}, Th_2Co_{17}, and $ThMn_{12}$, although all representing different classes, are related. These structures are based on the $MgZn_5$ lattice in which thorium replaces magnesium and the transition element replaces zinc. By systematically replacing particular
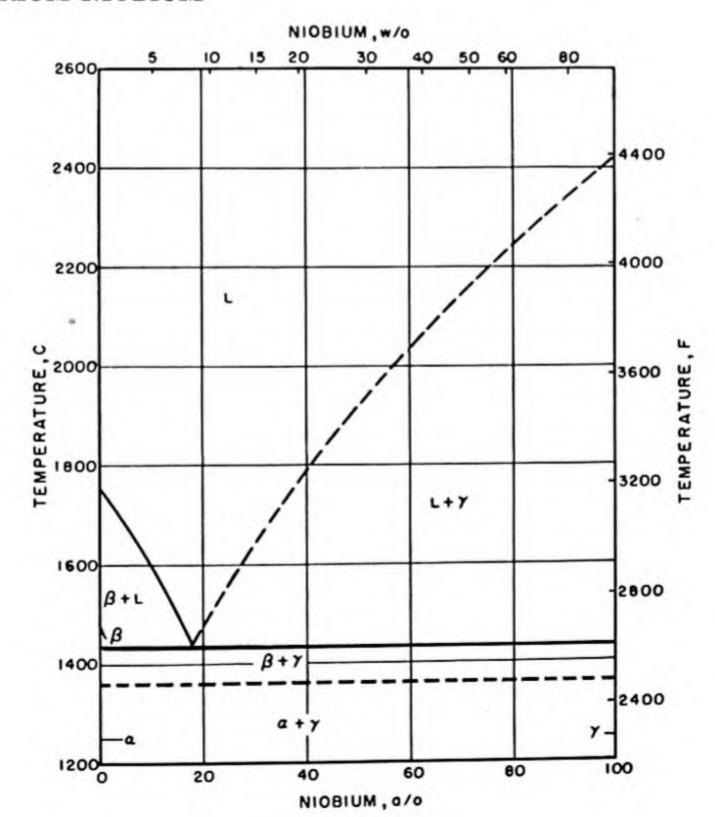
| Phase | Unit cell | | | Density, g/cm³ | | Space group | Remarks |
	Type	Dimensions, A	Number of molecules	X-ray	Other		•
Gamma (Th_7Ni_3)	Hexagonal	$a = 9.86$ $c = 6.23$	2			C6mc	Isomorphous with Th_7Fe_3 and Th_7Co_3
Delta (ThNi)	Orthorhombic	$a = 14.51$ ± 0.04 $b = 4.31$ ± 0.02 $c = 5.73$ ± 0.02	8			Pn2a or Pnma	
Epsilon ($ThNi_2$)	Hexagonal	$a = 3.95$ $c = 3.83$				P6/mmm	AlB₂-type structure, isomorphous with $ThCu_2$
Zeta ($ThNi_5$)	Hexagonal	$a = 4.97$ $c = 4.01$	1			C6m2, C6mm, or C6/mmm	Isomorphous with $CaZn_5$, $ThFe_5$, and $ThCo_5$
Eta (Th_2Ni_{17}	Hexagonal	$a = 8.37$ $c = 8.14$	2			C6/mmc, C6mc, or C6̄2c	

thorium atoms with pairs of transition-element atoms, the superlattices of hexagonal Th_2Ni_{17}, monoclinic Th_2Fe_{17} and Th_2Co_{17}, and body-centered tetragonal $ThMn_{12}$ can be derived.

References

1. L. HORN and C. WASSERMAN, *Z. Metallkunde*, **39**, 273 (1948).

2. H. A. WILHELM, O. N. CARLSON and A. I. SNOW, Progress Report in Metal-lurgy, ISC-6, 75–77 (May 1, 1947).

3. V. F. FLORIO, N. C. BAENZIGER and R. E. RUNDLE, "Compounds of Thorium With Transition Metals II. Systems With Iron, Cobalt, and Nickel," *Acta Cryst.*, **9**, 367–72 (1956).

4. J. R. MURRAY, "The Crystal Structure of Some Thorium Compounds," *J. Inst. Metals*, **4**, 91–6 (1955).

THORIUM-NIOBIUM

THE CONSTITUTIONAL DIAGRAM

The diagram which is shown has been determined by Carlson [1]. The diagram is based on metallographic examination, resistance measurements, thermal analyses, and x-ray diffraction experiments.

There are no compounds in the system, and a eutectic occurs at 1435 C and 8 w/o niobium. Solid solubility is very limited in all of the terminal phases. The maximum solubility in thorium is probably less than 1 w/o niobium at 1435 C.

The lattice constants of alpha thorium are lowered from 5.089 to 5.086 A by additions of niobium. The data indicate that probably much less than 0.1 w/o niobium is soluble in alpha thorium.

High-temperature x-ray experiments indicated that the beta-to-alpha transformation in thorium appears to be lowered slightly by niobium.[1] Chiotti [2, 3] reports that niobium getters thorium and that carbon raises the transformation temperature. On this basis, it appears that the effect of niobium may be largely the result of removal of carbon from solid solution.

CRYSTALLOGRAPHY

There are no compounds in the thorium-niobium system.

References

1. O. N. CARLSON, J. M. DICKINSON, H. E. LUNT and H. A. WILHELM, "Thorium-Columbium and Thorium-Titanium Alloy Systems," *J. Metals*, **8**, 132–36 (1956).
2. PREMO CHIOTTI, unpublished information (November, 1953).
3. PREMO CHIOTTI, private communication (March, 1954).

THORIUM-NITROGEN

There are two thorium nitrides formed: ThN [1] and Th_2N_3 [2, 3]. The mononitride, ThN, is stable to quite high temperatures, even under vacuum. Its melting point is 2630 ± 50 C. The sesquinitride, Th_2N_3, is not stable at 1500 C under vacuum.[2] Both nitrides are reported to react slowly at room temperature with oxygen and moisture from the air to form ThO_2.[4]

Early reports of Th_3N_4 are probably attributable to the identification of ThN or Th_2N_3. In at least one case, a lattice constant identical with that of ThN was reported.

The solubility of nitrogen in thorium has been determined.[4] Over the temperature range 845 to 1490 C the solubility is expressed by the following equation: $\log_{10}$ (nitrogen, w/o) $= -2405\ T + 0.9115$.

CRYSTALLOGRAPHY

The mononitride, ThN, has the NaCl structure. The tabulated data are from Rundle [1]. Chiotti [2] reports a lattice constant of $a = 5.144$ A for fused ThN.

The tabulated data for Th_2N_3 are from Zachariasen [3]. Chiotti [2] has reported similar results, giving $a = 3.87$ and $c = 6.16$ A.

Phase	Unit cell		Number of molecules	Density, g/cm³		Space group	Remarks
	Type	Dimensions, A		X-ray	Other		
ThN	Fcc	$a = 5.20$	4	11.56			NaCl-type structure, isomorphous with ThC, UC, UO, and UN
Th_2N_3	Hexagonal	$a = 3.875$ ± 0.002 $c = 6.175$ ± 0.004	1			C3̄m	La_2O_3-type structure

References

1. R. E. RUNDLE, "A New Interpretation of Interstitial Compounds," *Acta Cryst.*, **1**, 180–87 (1948).

2. PREMO CHIOTTI, "Experimental Refractory Bodies of High-Melting Nitrides, Carbides, and Uranium Dioxide," *J. Am. Cer. Soc.*, **35**, 123–30 (1952).

3. W. H. ZACHARIASEN, "The Crystal Structure of Th_2N_3," AECD-2090 (January 19, 1948).

4. A. F. GERDS and M. W. MALLETT, *J. Electrochem. Soc.*, **101**, 175–80 (1954).

THORIUM-OSMIUM

A compound $ThOs_2$ has been identified.[1] No other data are available.

CRYSTALLOGRAPHY

The structure of ThO_2 is given below. [1]

Phase	Unit cell		Number of molecules	Density, g/cm³		Space group	Remarks
	Type	Dimensions, A		X-ray	Other		
$ThOs_2$	Cubic	$a = 7.7050$	8			Fd3m	$MgCu_2$-type structure

Reference

1. A. E. DWIGHT, J. M. DOWNEY and R. A. CONNER, JR., "The Laves Phases $ThOs_2$ and $ThIr_2$," submitted to *J. Metals* (October 7, 1957).

THORIUM-OXYGEN

There appears to be only one stable oxide, ThO_2.[1] It is reported to have a melting point of 3300 ± 100 C.[3]

The solubility of oxygen in thorium is very limited [1]. Iodide thorium samples, analyzed before and after reaction with oxygen at 1415 C for 3 hr, contained 0.028 ± 0.003 w/o oxygen indicating that the thorium was originally saturated in oxygen. Consequently, this value represents an upper limit for oxygen solubility at 1415 C.[2]

CRYSTALLOGRAPHY

Thorium dioxide, ThO_2, has the fluorite structure and is completely soluble with UO_2. Solid solutions of the two oxides obey Vegard's law.[3, 4]

The data tabulated below are from Zachariasen [5]. Slowinski [4] reports similar data, giving $a = 5.586$ A, while Lambertson [3] reports a lattice constant of $a = 5.5961 ± 0.001$ A for ThO_2

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
ThO_2	Cubic	$a = 5.5859$ ± 0.0005	4				Fluorite structure, isomorphous with UO_2, NpO_2, PuO_2, and AmO_2

References

1. Brown-Firth Research Laboratories, United Kingdom, unpublished information (March, 1948).

2. A. F. GERDS and M. W. MALLETT, *J. Electrochem. Soc.*, **101**, 171–74 (1954).

3. W. A. LAMBERTSON, M. H. MUELLER and F. H. GUNZEL, JR., "Uranium Oxide Phase Equilibrium Systems," *J. Am. Cer. Soc.*, **36**, 397–99 (1953).

4. EMIL SLOWINSKI and NORMAN ELLIOTT, "Lattice Constants and Magnetic Susceptibilities of Solid Solutions of Uranium and Thorium Dioxides," *Acta Cryst.*, **5**, 768–70 (1952).

5. W. H. ZACHARIASEN, "Crystal Radii of the Heavy Elements," *Phys. Rev.*, **73** (9), 1104–05 (1948).

THORIUM-PHOSPHORUS

There is evidence of at least two thorium-phosphorus compounds. Meisel [1] examined thorium-phosphorus materials ranging from $ThP_{0.4}$ to $ThP_{1.33}$ and reported a subphosphide, composition unknown, and the phosphide Th_3P_4.

CRYSTALLOGRAPHY

The tabulated data are from Meisel [1]. Zumbusch [2] has shown that U_3P_4 is isomorphous with Th_3P_4 and that UP, which has the NaCl structure, is isomorphous with the thorium subphosphide.

| Phase | Unit cell | | | Density, g/cm^3 | | Space group | Remarks |
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Subphosphide	Fcc	$a = 5.818$ ± 0.003					Composition unknown
Th_3P_4	Bcc	$a = 8.600$ ± 0.002	4	8.56	8.44	$I\bar{4}3d$	

References

1. KARL MEISEL, "The Structure of Thorium Phosphides," Z. anorg. u. allgem. Chem., **240**, 300–12 (1939).
2. MARIA ZUMBUSCH, "Structural Analogy of Uranium and Thorium Phosphides," Z. anorg. u. allgem. Chem., **245**, 402–08 (1941).
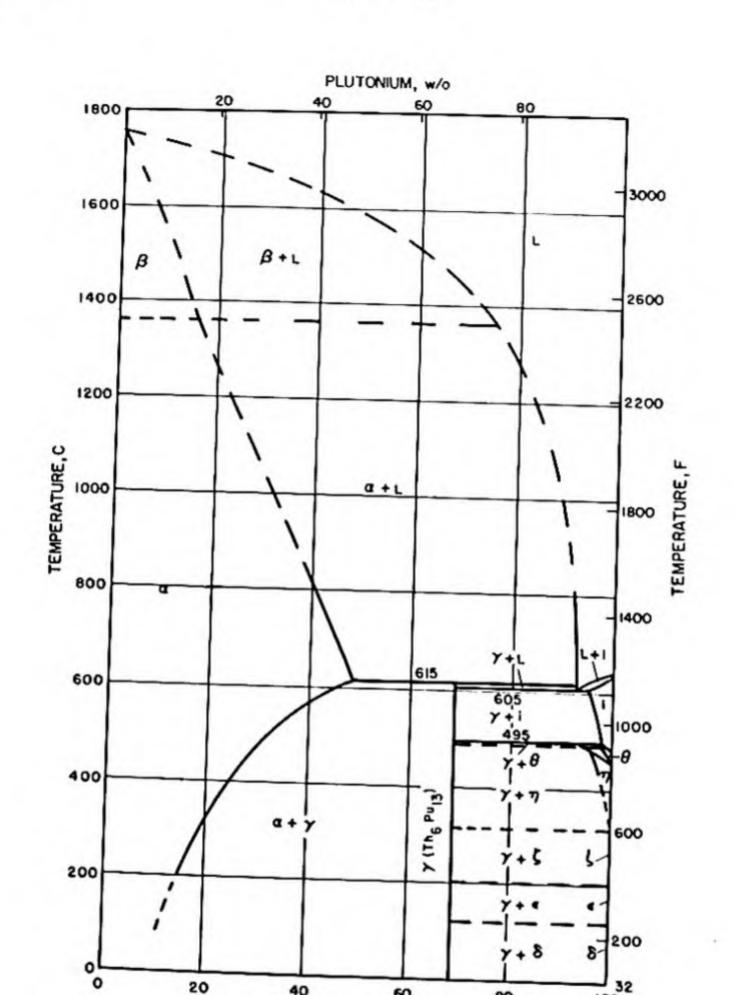
THORIUM-PLUTONIUM

THE CONSTITUTIONAL DIAGRAM

The diagram shown is from Poole, Williamson, and Marples [1]. It was derived from x-ray, metallographic, dilatometric, and thermal-analysis data.

Plutonium dissolves extensively in alpha thorium, as shown, but no data for plutonium solubility in beta thorium were obtained. Very approximate studies of the liquidus suggest that it is nearly horizontal in the region zero to 50 a/o plutonium and subsequently falls very steeply to the eutectic at 605 C and approximately 93 a/o plutonium.

A maximum solubility of 5 a/o thorium in the eta (delta plutonium) and iota (epsilon plutonium) phases is given. Solubility of thorium in the delta,

epsilon, and zeta phases (alpha, beta, and gamma plutonium, respectively) is believed to be small, but phase relationships below 440 C have not been investigated. The eta phase is retained at room temperature, however, even after cooling at 3 C/min.

The formation of gamma, Th_6Pu_{13}, is very sluggish on cooling. Alloys solidified under normal cooling rates were observed to contain alpha thorium and iota (epsilon plutonium). Gamma forms subsequently on annealing at about 550 C.

CRYSTALLOGRAPHY

| Phase | Unit cell | | | Density, g/cm³ | | Space group | Remarks |
	Type	Dimensions, Å	Number of molecules	X-ray	Other		
Gamma (Th₆Pu₁₃)	Ortho-rhombic	$a = 9.820$ $b = 8.164$ $c = 6.681$	1	13.96	14.0		

Reference
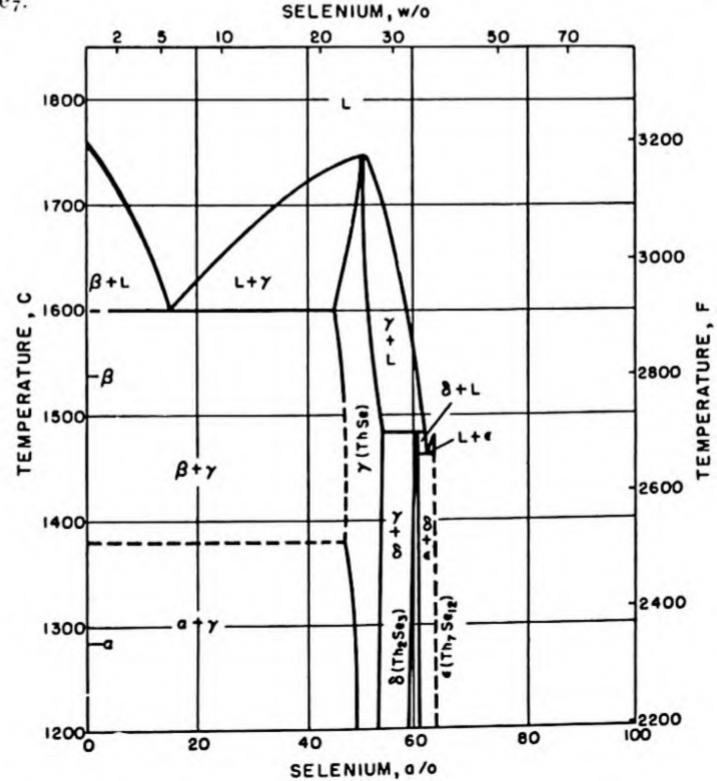
1. D. M. POOLE, G. K. WILLIAMSON and J. A. C. MARPLES, AERE M/R 2156 (1957); *J. Inst. Metals*, **86**, 172–76 (December, 1957).

THORIUM-SELENIUM

THE CONSTITUTIONAL DIAGRAM

According to D'Eye [1], there are five intermetallic compounds in the thorium-selenium system. These are $ThSe$, Th_2Se_3, Th_7Se_{12}, $ThSe_2$, and Th_3Se_7.

A portion of the system is shown in the accompanying diagram [1]. The thorium used in this work contained up to 0.5 w/o oxygen, and ThOSe was present. Except for the composition range $ThSe_{0.7}$ to $ThSe_{1.1}$, ThOSe was observed as a discrete phase and probably does not affect the diagram appreciably.[1]

The diagram shown is based on experiments in which a variety of techniques were utilized.

CRYSTALLOGRAPHY

The crystallography of the thorium selenides is summarized in the accompanying tabulation. No data are available for Th_3Se_7, although crystals of this compound were isolated by subliming selenium from selenium-rich samples.

The structure of ThOSe, which was present as an extraneous phase in part of the work, is tetragonal with $a = 4.038 \pm 0.005$ A, and $c = 7.019 \pm 0.005$ A. It has two molecules per unit cell in the space group P4/nmm, PbFCl-type structure.

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Gamma (ThSe)	Fcc	$a = 5.875 \pm 0.002$	4				NaCl-type structure
Delta (Th_2Se_3)	Ortho-rhombic	$a = 11.34 \pm 0.05$ $b = 11.57 \pm 0.05$ $c = 4.27 \pm 0.01$	4				Sb_2S_3-type structure
Epsilon (Th_7Se_{12})	Hexag-onal	$a = 11.569$ $c = 4.23 \pm 0.01$	1			P63/m	Isomorphous with Th_7S_{12}
Zeta ($ThSe_2$)	Ortho-rhombic	$a = 4.420 \pm 0.002$ $b = 7.610 \pm 0.002$ $c = 9.064 \pm 0.002$	4			Pmnb	Isomorphous with ThS_2
Eta (Th_3Se_7)	No data avail-able						

References

1. R. W. M. D'EYE, P. G. SELLMAN and J. R. MURRAY, "The Thorium-Selenium System," *J. Chem. Soc.* (London), 2555–62 (1952).
2. R. W. M. D'EYE, "The Crystal Structures of $ThSe_2$ and Th_7Se_{12}," *J. Chem. Soc.* (London), 1670–72 (1953).

THORIUM-SILICON

There is evidence of at least four intermetallic compounds in the thorium-silicon system. Zachariasen [1] reports alpha and beta $ThSi_2$ and Th_3Si_2 while Brauer [2] has reported only the alpha $ThSi_2$ compound. Jacobson [3] reports Th_3Si_2 in addition to the three forms given by Zachariasen.

There is a eutectic at the thorium end of the system. Foote [4] gives its location as 10 a/o silicon at a temperature above 1300 C.
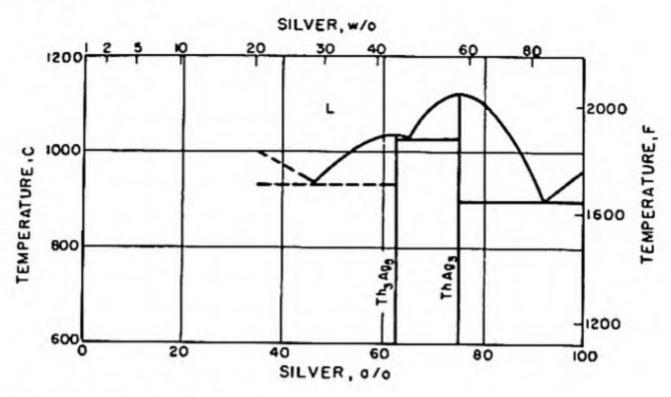
CRYSTALLOGRAPHY

The data for alpha $ThSi_2$ are from Brauer [2], for beta $ThSi_2$ from Zachariasen [1], and for ThSi and Th_3Si_2 from Jacobson [3].

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, Å	Number of molecules	X-ray	Other		
Alpha $ThSi_2$	Bc tetragonal	$a = 4.126$ $c = 14.346$	4	7.79	7.63	I4/amd	Isomorphous with alpha USi_2
Beta $ThSi_2$	Hexagonal	$a = 3.986$ $c = 4.227$					Appears to be similar to beta USi_2
Th_3Si_2	Tetragonal	$a = 7.835$ $c = 4.154$	4			P4/mbm	Isomorphous with U_3Si_2 and Th_3Al_2
ThSi	Orthorhombic	$a = 5.89$ $b = 7.88$ $c = 4.15$	4			Pbnm	Isomorphous with FeB, USi, PuSi

References

1. W. H. ZACHARIASEN, unpublished information (August, 1953).
2. G. BRAUER and A. MITIUS, "The Crystal Structure of $ThSi_2$," *Z. anorg. u. allgem. Chem.*, **249**, 325–39 (1942).
3. E. L. JACOBSON, R. D. FREEMAN, A. G. THARP and A. W. SEARCY, "Preparation, Identification, and Chemical Properties of the Thorium Silicides," *J. Am. Chem. Soc.*, **78**, 4850 (1956).
4. F. FOOTE, Metallurgy Division Progress Report, CT-2794 (March 27, 1945).

THORIUM-SILVER

SILVER, w/o

THE CONSTITUTIONAL DIAGRAM

The portion of this system which is shown is from Raub [1]. An additional pyrophoric thorium-rich compound, Th_2Ag, is reported by Murray [2].

The solid solubility in silver is less than 0.2 w/o thorium.[1]

The compound Th_3Ag_5 is pyrophoric.[1]

CRYSTALLOGRAPHY

The crystal structure of Th_2Ag has been reported by Murray [2].

Phase	Unit cell			Density, g/cm³		Space group	Remarks
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Th_2Ag	Tetrag-onal	$a = 7.56$ $c = 5.84$	4			I4/mcm	Isomorphous with $CuAl_2$, Th_2Al, and Th_2Au

References

1. E. RAUB, Z. *Metallkunde*, 40 (1949).

2. J. R. MURRAY, "The Crystal Structure of Some Thorium Compounds," *J. Inst. Metals*, 4, 91–6 (1955).

THORIUM-SODIUM

A partial diagram has been reported for this system by Grube and Botzenhardt [1] which showed extensive solubility of thorium in sodium and the presence of an intermetallic compound. Later work by Kelman [2] has shown, however, that this early work is in error. Numerous tests show that thorium is not attacked by sodium at temperatures of 650 to 800 C or by sodium-potassium mixtures at temperatures from 300 to 900 C [2[.

CRYSTALLOGRAPHY

It is uncertain whether compounds may exist in this system.

References

1. G. GRUBE and L. BOTZENHARDT, "The Alloys of Thorium With Copper, Aluminum, and Sodium," *Z. Elektrochem.*, **48**, 422 (1942).
2. L. KELMAN, private communication (1955).

THORIUM-SULFUR

Four sulfides of thorium have been identified: ThS, Th_2S_3, Th_7S_{12}, and ThS_2.[1, 2] The sulfide Th_7S_{12} is reported to have solubility limits of $ThS_{1.71}$ to $ThS_{1.76}$. The melting points of the sulfides are as follows:

ThS	2200 C
Th_2S_3	1950 ± 50 C
Th_7S_{12}	1770 ± 30 C
ThS_2	1905 ± 30 C

No other data on the constitution of this system are available.

CRYSTALLOGRAPHY

The crystallography of the thorium sulfides has been studied by Zachariasen [2, 3] and is tabulated below.

A report in the literature [4], indicating a sulfide of $ThS_{0.5}$ to $ThS_{0.75}$ with a defect NaCl structure, has been shown to be in error. Zachariasen [2] has shown that $ThS_{0.835}$ contains metallic thorium and that the monosulfide is characterized by a thorium-sulfur ratio of 1.0.

The lattice constants of the sulfide Th_7S_{12} have been shown to vary with composition over the range $ThS_{1.71}$ to $ThS_{1.76}$. The data indicate that this is a defect structure from which thorium atoms can be removed

Phase	Unit cell			Density, g cm³		Space group	Remarks
	Type	Dimensions, Å	Number of molecules	X-ray	Other		
ThS	Fcc	$a = 5.682$ ± 0.002	4	9.56			Isomorphous with US and CeS
Th_2S_3	Ortho-rhombic	$a = 10.99$ ± 0.05 $b = 10.85$ ± 0.05 $c = 3.96$ ± 0.03	4	7.87		Pbnm	Sb_2S_3-type structure, isomorphous with Np_2S_3 and U_2S_3
Th_7S_{12}	Hexag-onal	$a = 11.063$ ± 0.001 $c = 3.991$ ± 0.001	1	7.88	7.73	$P6_3$ m	
ThS_2	Ortho-rhombic	$a = 4.268$ ± 0.002 $b = 7.264$ ± 0.003 $c = 8.617$ ± 0.003	4	7.36		Pmnb	$PbCl_2$-type structure

without destroying the stability of the phase. There is not room for more than 12 sulfur atoms per unit cell [3].

D'Eye [5] has shown that the thorium sulfides are isomorphous in each case with corresponding selenides. An additional polyselenide, Th_3Se_7, to which no sulfide corresponds, was found.

References

1. E. D. EASTMAN, LEO BREWER, L. A. BROMLEY, P. W. GILLES and N. L. LOFGREN, "Preparation and Properties of the Sulfides of Thorium and Uranium," *J. Am. Chem. Soc.*, **72**, 4019-23 (1950).

2. W. H. ZACHARIASEN, "Crystal Chemical Studies of the 5f-Series of Elements X. Sulfides and Oxysulfides," *Acta Cryst.*, **2**, 291-96 (1949).

3. W. H. ZACHARIASEN, "Crystal Chemical Studies of the 5f-Series of Elements IX. The Crystal Structure of Th_7S_{12}," *Acta Cryst.*, **2**, 288-91 (1949).

4. E. F. STROTZER and M. ZUMBUSCH, *Z. anorg. u. allgem. Chem.*, **247**, 415 (1941).

5. R. W. M. D'EYE, P. G. SELLMAN and J. R. MURRAY, "The Thorium-Selenium System," *J. Chem. Soc.* (London), 2555-62 (1952).

THORIUM-TANTALUM

Wilhelm [1] examined thorium and tantalum after reaction at 2000 C and found only alpha thorium, tantalum and thorium dioxide by x-ray diffraction examination. Similar results are reported by Murray and Thomas [2].

Wilhelm reports that the solubility of thorium in tantalum is quite limited. This report is based on a determination of the lattice coefficients of the tantalum solid solution. No reliable data are available on the solubility of tantalum in thorium. Chiotti [3] reports that thorium is gettered by additions of tantalum.

CRYSTALLOGRAPHY

No intermetallic compounds occur in this system.

References

1. H. A. WILHELM, A. S. NEWTON, A. H. DAANE and C. NEHER, "Thorium Metallurgy," CT-3714 (February, 1946).
2. J. R. MURRAY and C. H. THOMAS, United Kingdom, unpublished information (1957).
3. P. CHIOTTI, private communication (March, 1954).

THORIUM-TELLURIUM

D'Eye [1] has reported the existence of three intermetallic compounds in this system ThTe, $ThTe_2$, and Th_3Te_8 which all decompose below 1000 C to thorium and tellurium.

An additional compound, nominally assigned the stoichiometry of Th_3Te has also been reported [2].

CRYSTALLOGRAPHY

No details are available for either $ThTe_2$ or Th_3Te_8; both gave complex diffraction patterns [1]. The structure of ThOTe which was present as an

| Phase | Unit cell | | | Density, g/cm³ | | Space group | Remarks |
	Type	Dimensions, A	Number of molecules	X-ray	Other		
ThTe	Cubic	$a = 3.826$	1			Pm3m	CsCl-type structure

extraneous phase is tetragonal with $a = 4.120$ and $c = 9.564$ A. It has two molecules per unit cell in the space group P4/nmn and is isostructural with ThOSe and ThOS.

References

1. R. W. M. D'EYE and P. G. SELLMAN, "The Thorium Tellurium System," *J. Chem. Soc.* (London), 3760 (1954).
2. E. MONTIGNIE, "Tellurides of Uranium, Thorium, and Cerium," *Bull. soc. chim.* (France), 748–49 (1947).

THORIUM-THALLIUM

The solubility of thorium in liquid thallium is reported to increase from 0.27 w/o at 800 C to 0.33 w/o at 900 C [1].

CRYSTALLOGRAPHY

No data are available.

Reference

1. E. E. HAYES and P. GORDON, *J. Met. and Cer.*, TID-65, 130–41 (July, 1948). Classified.

THORIUM-TIN

The solubility of thorium in liquid tin has been reported as follows: less than 0.05 w/o, 600 C; 0.2 w/o, 700 C; 1.9 w/o, 800 C; and 4.3 w/o, 900 C.
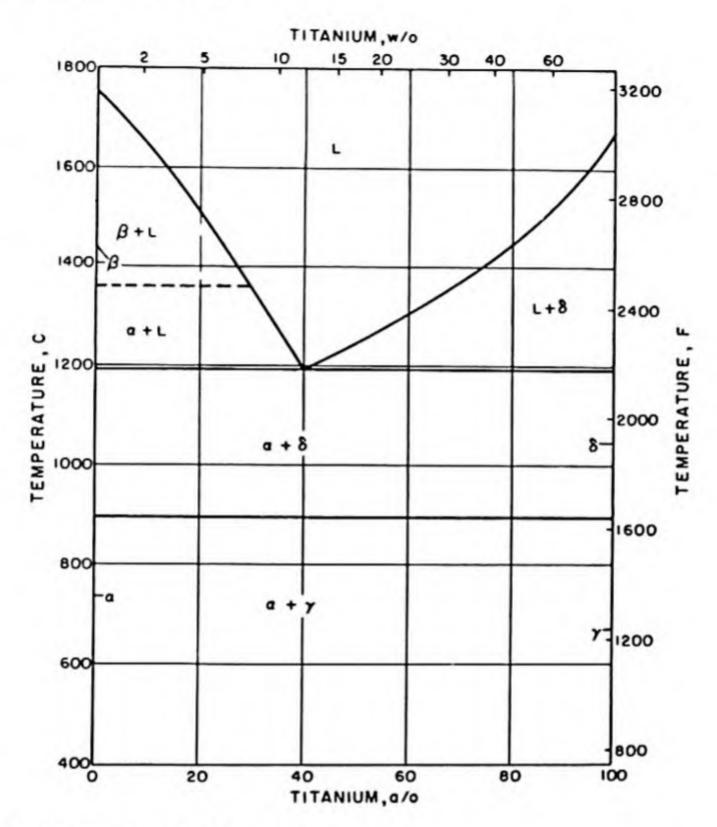
CRYSTALLOGRAPHY

No data concerning compounds in this system are available.

Reference

1. E. E. HAYES and P. GORDON, *J. Met. and Cer.*, TID-65, 130–41 (July, 1948). Classified.

THORIUM-TITANIUM

THE CONSTITUTIONAL DIAGRAM

The diagram which is shown has been determined by Carlson [1]. It is based on experiments utilizing a variety of methods. These include x-ray diffraction, metallographic examination, thermal analyses, and diffusion experiments.

There are no compounds in this system. A eutectic is formed at 1190 C and 12 w/o titanium. It is reported that the transformation in titanium is unaffected by additions of thorium.[1]

Lattice constants were determined for alloys in this system. The data indicate that the solubility in thorium is probably less than 0.1 w/o titanium, and the solubility of thorium in titanium is even less.[1]

Since the solubility of titanium in thorium is slight, there is probably little effect of titanium on the transformation of thorium from alpha to beta. Chiotti [2] reports that titanium getters thorium.

CRYSTALLOGRAPHY
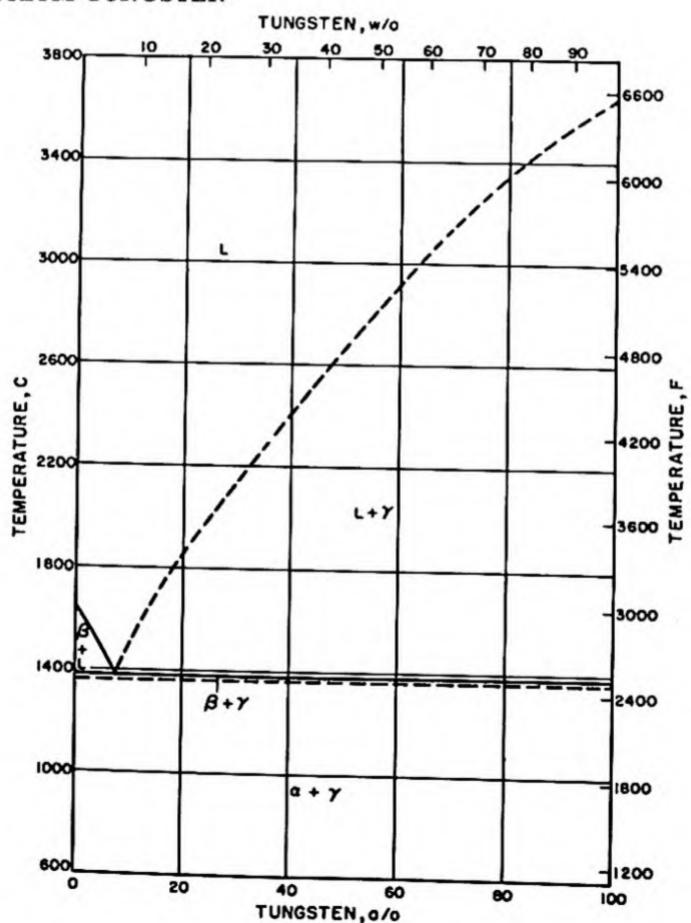
There are no compounds in the thorium-titanium system.

References

1. O. N. CARLSON, J. M. DICKINSON, H. E. LUNT and H. A. WILHELM. "Thorium-Columbium and Thorium-Titanium Alloy Systems," *J. Metals,* 8, 132-36 (1956).

2. PREMO CHIOTTI, private communication (March, 1954).

THORIUM-TUNGSTEN

THE CONSTITUTIONAL DIAGRAM

The diagram which is shown was determined by Lloyd and Murray [1]. It is based on studies in which a variety of experimental techniques were used. There is little solubility in any of the terminal phases.

This is in general agreement with earlier work of Wilhelm [2], who reported that there were no intermetallic compounds in the system and that the eutectic temperature was 1475 C.

CRYSTALLOGRAPHY

No compounds occur in this system.

References

1. S. J. LLOYD and J. R. MURRAY, United Kingdom, unpublished information (1955).

2. H. A. WILHELM, A. S. NEWTON, A. H. DAANE and C. NEHER, "Thorium Metallurgy," CT-3714 (February, 1946).
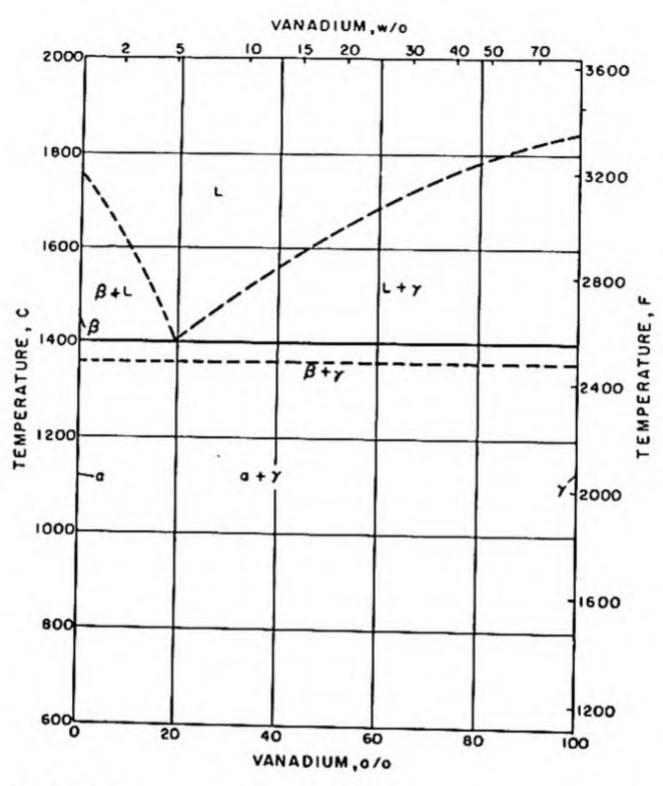
THORIUM-VANADIUM

THE CONSTITUTIONAL DIAGRAM

The diagram which is shown has been reported by Levingston and Rogers [1]. It is based on studies in which a variety of experimental techniques was used.

There are no compounds in this system. The eutectic reaction is indicated as occurring at 1400 C and 19 a/o (5 w/o) vanadium [1], although in a more recent determination [2] the eutectic temperature is reported as 1420 C. Vanadium has little effect on the transformation of thorium from alpha to beta [1], the transformation being given as 1360 C in thorium-vanadium alloys.[2]

There is little solubility in any of the terminal phases in this system. A specimen of thorium had a lattice parameter of $a = 5.087 \pm 0.002$ A when furnace cooled and examined by x-ray diffraction. Specimens of thorium quenched from 1300 C gave a lattice parameter of $a = 5.094 \pm 0.004$ A. This parameter indicates that only a slight solubility of vanadium in thorium occurs even at high temperatures.[1]

CRYSTALLOGRAPHY

There are no intermetallic compounds in this system.

References

1. H. L. LEVINGSTON and B. A. ROGERS, "The Thorium-Vanadium System," AECD-3602 (April 22, 1953).

2. H. A. WILHELM, "Nuclear Fuels Newsletter," WASH-704 (December, 1957). Classified.

THORIUM-ZINC

Wilhelm [1] has reported a compound, Th_2Zn. It is stable to 1040 C, at which temperature it decomposes to form thorium and zinc.

Data are incomplete for the system from Th_2Zn to zinc. However, Nowotny [2] has reported that a compound, $ThZn_9$, is formed.

CRYSTALLOGRAPHY

Baenziger has reported the data for Th_2Zn, and Nowotny the data for $ThZn_9$ given below.

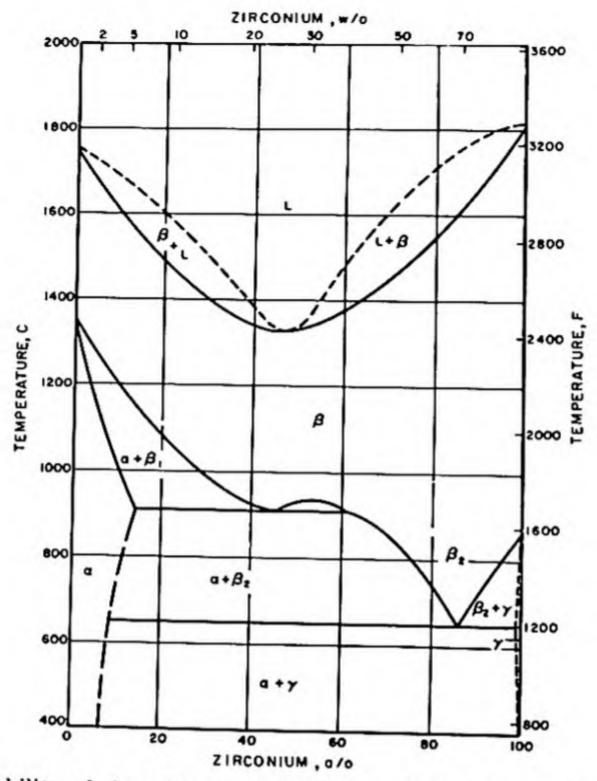| Phase | Unit cell | | | Density, g/cm³ | | Space group | Remarks |
	Type	Dimensions, A	Number of molecules	X-ray	Other		
Th_2Zn	Bc tetragonal	$a = 7.60$ $c = 5.64$	4	10.6		I4/mcm	Isomorphous with $CuAl_2$, Th_2Al, Th_2Au, Th_2Cu
$ThZn_9$	Hexagonal	$a = 5.24$ $c = 4.45$	1			P6/mmm	Isomorphous with $CaZn_5$, $ThFe_5$, $CeZn_5$

References

1. H. A. WILHELM, A. S. NEWTON, A. H. DAANE and C. NEHER, "Thorium Metallurgy," CT-3714 (February, 1946).

2. H. NOWOTNY, "Crystal Structure of $ThZn_9$, Cd_2Ca, and $(AgMg)_2Ca$," *Metallforschung*, **1**, 31–34 (1946).

3. N. C. BAENZIGER, R. E. RUNDLE and A. I. SNOW, "Structure of the Compounds Th_2Cu, $ThCu_2$, Th_2Zn, and $ThHg_3$," *Acta Cryst.*, **9**, 93 (1956).

THORIUM-ZIRCONIUM

THE CONSTITUTIONAL DIAGRAM

The diagram shown is from Carlson [1, 2]. It is confirmed in part by the work of Saller and Rough [3]. The eutectoid at the zirconium end of the system occurring at 650 C and 14.7 a/o thorium and the minimum in the liquidus is confirmed by Murray [4].

The $beta_1$-plus-$beta_2$ loop shown is based on high-temperature x-ray studies of alloys prepared from sponge thorium and crystal-bar zirconium. Attempts to retain a two-phase microstructure by quenching from within the loop were unsuccessful.[2] Similarly, Murray [4] reports that no evidence of the $beta_1$-plus-$beta_2$ was obtained metallographically in alloys made by arc melting crystal-bar thorium and zirconium. However, in alloys prepared from bar-stock thorium the existence of a small $beta_1$-plus-$beta_2$ field with a maximum composition and temperature range of 38 to 65 a/o zirconium and 915 to 950 C, respectively, was observed. These results seem to indicate that in pure binary alloys the immiscibility loop tends to close.
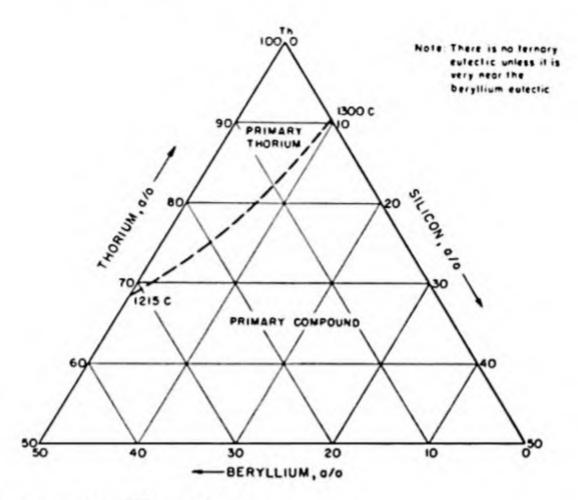
The solubility of zirconium in alpha thorium is based on lattice-parameter measurements [2]. The solubility of thorium in gamma (alpha zirconium) is less than 2.2 a/o.[5]

CRYSTALLOGRAPHY

There are no compounds in the thorium-zirconium system.

References

1. O. N. CARLSON, "Some Studies of the Uranium-Thorium-Zirconium Ternary System," AECD-3206 (June 5, 1950).

2. E. D. GIBSON, B. A. LOOMIS and O. N. CARLSON, "Thorium-Zirconium and Thorium-Hafnium Alloy Systems," *Trans. ASM*, 50 (1958).

3. H. A. SALLER and F. A. ROUGH, "Proceedings of Spring Metallurgy Conference," TID-5084 (March, 1952). Classified.

4. J. R. MURRAY, United Kingdom, unpublished information (1956).

5. P. C. L. PFEIL, "A Discussion of the Factors Affecting the Constitution of Zirconium Alloys," AERE M/R 960 (June 27, 1952).

THORIUM-BERYLLIUM-SILICON
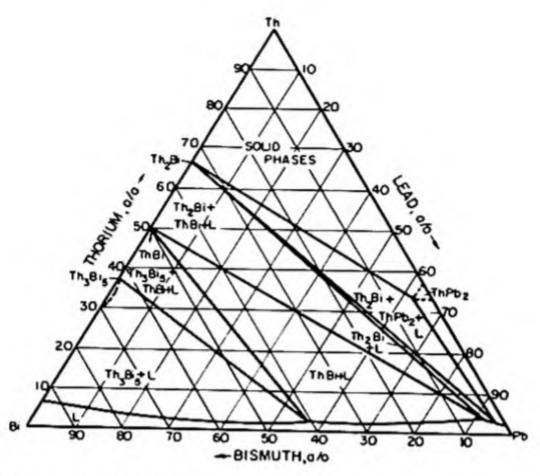

THE CONSTITUTIONAL DIAGRAM

A portion of the liquidus of the thorium-rich alloys has been reported.[1] There is a eutectic trough which slopes from a maximum greater than 1300 C at the thorium-silicon eutectic to the thorium-beryllium eutectic at 1215 C.[2]

CRYSTALLOGRAPHY

No new phases are involved in the ternary system.

References

1. F. FOOTE, Metallurgy Division Progress Report, CT-2794 (April, 1945).

2. H. A. WILHELM, A. S. NEWTON, A. H. DAANE and C. NEHER, "Thorium Metallurgy," CT-3714 (February, 1946).

THORIUM-BISMUTH-LEAD

THE CONSTITUTIONAL DIAGRAM

An isothermal section determined at 1000 C by Bryner [1] is shown in the accompanying figure. As noted in the thorium binary-diagram section, Ferro [2] has identified the compound shown here as Th_3Bi_5 as Th_3Bi_4. Consequently, some revision in the diagram shown is undoubtedly required. However, since exact details are unknown, the diagram has been reproduced as orginally determined.

Lead lowers the solubility of thorium in bismuth.

CRYSTALLOGRAPHY

No new phases are involved in the thorium-bismuth-lead system.

References

1. J. S. BRYNER and R. J. TEITEL, private communication (1956).
2. R. FERRO, Acta Cryst., 10, 476 (1957).